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Laser Flash Photolytic Determination of Quenching
Rate Constants for Triplet Sensitizers by Alkyl Peroxides

by

Treacy Lynn Woods

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Paul S. Engel, Professor of Chemistry

Edward S. Lewis, Professor of Chemistry

Barry F. Dunning, Associate Professor of Space Physics

HOUSTON, TEXAS

APRIL, 1983
ABSTRACT

Laser Flash Photolytic Determination of Quenching
Rate Constants for Triplet Sensitizers by Alkyl Peroxides

by

Treacy L. Woods

Rate constants for quenching of triplet sensitizers by several alkyl peroxides were measured by laser flash photolysis in benzene solution. Because these rate constants decrease monotonically with sensitizer triplet energy, electronic energy transfer is concluded to be the likely quenching mechanism. A rough correlation exists between quenching rate constants and peroxide thermal lability. Finally, the computer interfaced laser flash photolysis apparatus which was used in these measurements is described in detail.
ACKNOWLEDGEMENTS

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INTRODUCTION

Photochemical triplet sensitized decomposition of acyl and alkyl peroxides has been known since 1955. The reactions involved are shown in Scheme I where S is the sensitizer and Q is the peroxide.

Scheme I

\[ S \xrightarrow{h \phi} S^* \]

\[ S^* \xrightarrow{k_f} S + h \phi_f \] (1)

\[ S^* \xrightarrow{k_d} S \] (2)

\[ S^* \xrightarrow{k_{isc}} S^{*3} \] (3)

\[ S^{*3} \xrightarrow{k_d'} S \] (4)

\[ S^{*3} \xrightarrow{k_p} S + h \phi_p \] (5)

\[ S^{*3} + Q \xrightarrow{k_q} Q^{*3} + S \] (6)

In step 7, the key step, peroxide quenches the triplet state with a rate constant referred to henceforth as \( k_q \). Quenching may be electronic energy transfer as shown or some other process such as electron transfer.

Sensitizers are compounds such as aromatic hydrocarbons and ketones which absorb uv light and form metastable excited electronic states. Although quenching of sensitizer triplets by many classes of compounds has been intensively studied, literature reports of the quenching process for peroxides are sparse. In this section, the general known facts will be reviewed and the proposed mechanisms will
be described. Then, a table of all the literature quenching rate constants will be presented. Finally, the aims of this thesis project will be described.

In 1965, Walling and Gibian\textsuperscript{2} published the first major study in this area. They monitored the photochemical decomposition of benzoyl peroxide (BP) and di-tert-butyl peroxide (DTBP) in the presence of sensitizers having triplet energies in the range of 42-73.6 kcal mol\textsuperscript{-1}. Sensitizers whose triplet energy ($E_T$) exceeded 55 kcal mol\textsuperscript{-1} were found to sensitize the decomposition of BP. The decomposition did not proceed with unit efficiency; in fact, the highest quantum yield ($\Phi$) observed for BP and benzophenone, a rather high energy sensitizer, was only 0.25. Typical quantum yields were in the range 0.05 to 0.25. Anthracene, ($E_T = 42.0$ kcal mol\textsuperscript{-1}), was an exception to the 55 kcal mol\textsuperscript{-1} cutoff in that it unexpectedly sensitized the decomposition of BP. The singlet state of anthracene, which has an energy of 75.4 kcal mol\textsuperscript{-1}, was probably responsible for its unusual potency.

Indeed, five years later, Nakata and Tokumaru\textsuperscript{3} proved the involvement of anthracene singlet in a study of BP photolysis in the presence of five aromatic hydrocarbons. Quantum yields of peroxide decomposition were measured with and without added 1,3-pentadiene, a known triplet quencher. Since the $\Phi$'s were the same in both cases, a singlet process was strongly implicated. In a separate experiment, a plot of the reciprocal of these $\Phi$'s versus reciprocal peroxide concentration was constructed, leading to a value for $k_q\tau$ where $k_q$ is the rate constant for the quenching of the hydrocarbon singlet state by the peroxide and $\tau$ is the singlet lifetime of the hydrocarbon without
peroxide. The $k_q$ values obtained from the quantum yield plots were in reasonable agreement with the $k_q$ values obtained from Stern-Volmer plots of fluorescence quenching by BP. This result argued strongly for a singlet process because it demonstrated that the sensitizing state has the same lifetime as the fluorescing state. Using the literature value for the lifetime of the anthracene singlet, Nakata and Tokumaru calculated a $k_q$ of $9.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for anthracene singlet. Hence, the quenching of anthracene singlet by BP is essentially a diffusion-controlled process and was surely occurring in Walling and Gibian's system.

Another important result of Walling and Gibian was that benzophenone failed to sensitize the decomposition of DTBP. It is unfortunate that the exact peroxide and sensitizer concentrations used in this experiment were not reported because quenching could be a slow process for DTBP. In that case, DTBP decomposition would not be seen unless its concentration was rather high.

Walling and Gibian suggested that the mechanism for sensitized decomposition of BP involved a slow nonvertical energy transfer process. They supported their proposal by noting that peroxides do not possess low-lying, spectroscopic, bound triplet states. Also, their $k_q$ value for the system benzophenone BP was at least 1000 times slower than the diffusion controlled limit. (See Table I on page 16).

In contrast to the DTBP result, benzophenone was found to sensitize tert-butyl hydroperoxide decomposition. Walling and Gibian point out that besides nonvertical energy transfer, some other mechanism involving abstraction of a hydrogen atom from hydroperoxide
by benzophenone triplet could be occurring. Since DTBP does not possess an easily abstractable hydrogen atom, it would be unreactive in such a mechanism.

F. G. Moses\textsuperscript{4} determined the products of the singlet and triplet sensitized decomposition of acetyl peroxide. Different product ratios were obtained from the triplet process compared with the singlet process.

W. F. Smith\textsuperscript{5} studied the benzophenone and 2-acetonaphthone triplet sensitized decomposition of BP in benzene. He measured quantum yields for peroxide disappearance ($\Phi_{-P}$) and for benzoic acid appearance ($\Phi_{A}$) at different initial concentrations of BP. The ratio of $\Phi_{A}/\Phi_{-P}$ indicated the types of mechanisms that could be operating in this system. For 2-acetonaphthone, $\Phi_{A}/\Phi_{-P}$ was essentially constant over a range of peroxide concentration. Hence, Smith concluded that quenching goes by energy transfer only for this sensitizer. For benzophenone, $\Phi_{A}/\Phi_{-P}$ varied with peroxide concentration, implying that besides energy transfer, another mechanism involving the benzophenone ketyl radical was occurring. The pertinent reactions are shown in equations 8–10.

\[
R_{1}R_{2}CO^{*3} + \text{C}_6\text{H}_6 \rightarrow R_{1}R_{2}CO + \text{C}_6\text{H}_5^{\cdot} \quad (8)
\]

\[
R_{1}R_{2}CO^{*3} + (\text{PhCOO})_2 \xrightarrow{\text{SH}} R_{1}R_{2}CO + \text{PhCOOH} + \text{other products} \quad (9)
\]

\[
R_{1}R_{2}CO^{\cdot} + (\text{PhCOO})_2 \rightarrow R_{1}R_{2}CO + \text{PhCOOH} + \text{other products} \quad (10)
\]

In step 10, peroxide is reduced by a sensitizer-derived radical and the
sensitizer is regenerated. This process is called chemical sensitization. From his quantum yield data and assumed triplet lifetimes, Smith calculated $k_q$ for his two sensitizers. (See Table I). The slope of the $\log k_q$ vs. triplet energy line between these two points was $-0.133$, which is much lower than the theoretical slope of $-0.733$ for energy transfer between spectroscopic triplets in the region where the process is not diffusion controlled. The low slope led him to suspect that nonvertical energy transfer was occurring. The rate constant for step 8 has since been determined by Schuster et. al. and has the value of only $16.4 \text{ M}^{-1}\text{sec}^{-1}$. Ketyl involvement is unimportant in Smith’s system. A calculation (see Appendix B) using Smith’s rate constant for step 9, Schuster’s rate constant for step 8, and the known lifetime of benzophenone triplet in benzene (10 µsec) shows that less than 1% of benzophenone triplets abstract hydrogen from the solvent benzene and form ketyl radicals at the maximum BP concentration (0.07 M) studied by Smith.

Smith and Rossister found that when benzophenone ketyl radical was generated under more favorable conditions, namely, upon irradiation of benzene solutions of benzophenone and benzhydrol, it induced the decomposition of BP by a radical chain mechanism.

Kuz’min and Guseva measured quantum yields for the triplet sensitized decomposition of acetyl peroxide by six aromatic ketones and one aromatic hydrocarbon. From their data, they calculated a $k_q$ value for benzophenone in heptane. (See Table I).

Kashiwagi, Fujimori, Kozuka, and Oae sensitized the decomposition of $\beta$-phenylisobutyryl peroxide (BPIP) with triplet
acetophenone in isooctane.

\[
\begin{align*}
\text{BPIP} \\
\text{The products for the triplet sensitized reaction with optically active peroxide and with }^{18}O \text{ labelled peroxide were reported but no rate constants were measured. Triplet energy transfer between sensitizer and peroxide was assumed.}
\end{align*}
\]

Maheshwari, de Mayo, and Wiegand\textsuperscript{13} were able to sensitize the rearrangement of ascaridole, ASC, to isoascaridole in dioxan with the triplet sensitizers Michler's ketone, triphenylamine, and phenanthrene.

\[
\begin{align*}
\text{\textsuperscript{h}ν} & \quad \text{s}^*3
\end{align*}
\]

Although the same reaction also occurred upon direct irradiation, it was accelerated in the presence of triplet sensitizers. No quenching studies were done to rule out involvement of the singlet; neither were any quantum yields or rate constants measured.

Leffler and Miley\textsuperscript{14} prepared some ketoperoxides in which the benzoyl peroxide and benzophenone sensitizer moieties were built into the same molecule. An example is p-BBP.
p-BBP

They measured the quantum yields for decomposition of the ketoperoxides; for example, $\Phi$ for p-BBP was 0.97. Intramolecular energy transfer therefore led to 100% efficient decomposition compared with only 25% efficiency in Walling and Gibian's benzophenone-BP intermolecular system. Leffler and Miley suggested that the reason for Walling and Gibian's low $\Phi$ is formation of a peroxide-sensitizer triplet exciplex (E), which decays to ground state peroxide (P) and sensitizer (S) much of the time.

$$S^* + P \rightarrow E$$
$$E \rightarrow P + S$$
$$E \rightarrow P^* + S$$

Fahrenholtz and Trozzolo$^{15}$ used chemically induced dynamic nuclear polarization (CIDNP) to show that triplet sensitized decomposition of BP goes through triplet radical pairs. They observed the correct CIDNP for triplet radical pairs with sensitizers possessing $E_T$'s exceeding 59 kcal mol$^{-1}$, in accord with the results of Walling and Gibian$^{2}$ and they saw no CIDNP with biacetyl or benzophenone. In general, triplet CIDNP occurred when three conditions were satisfied: 1) the sensitizer had sufficient triplet energy; 2) the sensitizer possessed a low fluorescence quantum yield; and 3) little
photoreduction occurred under the experimental conditions. Photoreduction occurs when triplet sensitizer abstracts a hydrogen atom from another molecule, such as solvent. Triplet sensitizers such as benzophenone and biacetyl which have $^3(n,n^*)$ lowest triplet states are known to undergo this process in the cyclohexane and n-butyl acetate solvents used in this study. Aromatic hydrocarbons with appreciable quantum yields for fluorescence gave CIDNP characteristic of singlet radical pairs rather than triplet radical pairs. Fahrenholtz and Trozzolo suspected that triplet biacetyl ($E_T = 55$ kcal mol$^{-1}$) was not sufficiently energetic to sensitize peroxide decomposition and give CIDNP under their experimental conditions.

While studying the photochemical alkylation of peptides, Schwarzberg, Sperling, and Elad$^{16}$ reported in 1973 the efficient triplet sensitized decomposition of DTBP by biacetyl. The reaction is:

Prior to 1973, they carried out this alkylation by irradiating mixtures
of acetone, toluene, and peptide. Acetone absorbed the light and its \( 3(n,\pi^*) \) state abstracted a hydrogen atom from the peptide, resulting in alkylation by a radical process. When the reaction was tried with biacetyl in place of acetone, alkylation did not occur. Elad and co-workers supposed that this was due to the poorer hydrogen atom abstracting ability of triplet biacetyl relative to acetone.\(^{17}\) DTBP was added to the system in the hope that biacetyl would absorb the light and transfer energy to DTBP which would then homolyze to tert-butoxy radicals. Indeed, alkylation yields of 10–50% were obtained in the presence of DTBP, with the best yield at a toluene:peroxide concentration ratio between 3:1 and 2:1.

Elad et al. proposed the mechanism shown in Scheme II and carried out three kinds of photochemical experiments to show that the tert-butoxy radicals came from the interaction of biacetyl triplet with DTBP.

Biacetyl was first found to be photochemically stable in the solvent, tert-butyl alcohol. When DTBP was added, biacetyl was destroyed. When toluene was added, biacetyl destruction slowed down and DTBP disappearance increased. Other compounds like 1-octene or peptide behaved similarly to toluene. These results implied that toluene scavenges tert-butoxy radicals which would otherwise destroy biacetyl.

For the system consisting of biacetyl, DTBP, and toluene, it was possible to suppress bibenzyl formation by adding sufficient 1-nitronaphthalene, a known quencher of biacetyl triplets. Bibenzyl is the recombination product of benzyl radicals formed by the reaction of
tert-butoxy radical and toluene. It was concluded from a linear Stern-Volmer plot that only one excited state was involved in tert-butoxy radical formation, namely, biacetyl triplet.

Scheme II

The quantum yield for DTBP decomposition during a peptide alkylation was found to be 0.67, a much higher value than Walling and Gibian's 0.25 for BP and benzophenone. The newer value is more in line with the unit quantum yield observed for the direct photolysis of DTBP\textsuperscript{18}. 
In view of Walling and Gibian's 59 kcal mol$^{-1}$ cutoff for BP, it is surprising that biacetyl ($E_T = 55$ kcal mol$^{-1}$) was able to sensitize DTBP decomposition in Elad's system since the more energetic benzophenone triplet did not sensitize DTBP decomposition in Walling and Gibian's system. The photochemical experiments of Elad and co-workers implicate biacetyl triplet in the production of tert-butoxy radicals from DTBP but energy transfer is not the only possible mechanism. Biacetyl ketyl radical, for example, could be involved in the chemical sensitization mechanism shown below.

Indeed, we have measured the lifetime of biacetyl ketyl radical in another alcoholic solvent, isopropanol, in which it is conveniently generated by flash photolysis. We have also measured $k_q$ for biacetyl ketyl radical and DTBP in isopropanol. (See Appendix B). A calculation (see Appendix B) shows that at Elad's toluene concentration (1.42 M) and DTBP concentration (0.274M) 14% of the biacetyl triplets abstract hydrogen from toluene and form ketyl radicals while 37% of the biacetyl triplets are quenched by DTBP via an energy transfer mechanism. This analysis assumes that our rate constants for
isopropanol are the same for Elad’s solvent, tert-butanol, and uses an estimated value for the rate constant for the abstraction of hydrogen from toluene by biacetyl \(1 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1}\)\(^\text{20}\) and a value for the lifetime of biacetyl triplet in isopropanol estimated from the work of Singh et. al.\(^\text{19}\) (20 μsec).

In 1978, Ng and Guillet\(^\text{24}\) reported quenching the Norrish Type II reaction of polymeric ketones with DTBP and tert-butyl hydroperoxide in benzene. Polymer chain scission quantum yields were measured and \(k_q\) for the quenching of polystyrene co-phenyl vinyl ketone (PS-PVK) triplet by DTBP was obtained from an appropriate Stern-Volmer plot. (See Table I). Although the Type II process goes through a biradical intermediate, Ng and Guillet concluded by circular reasoning that peroxide quenched the triplet not the biradical, because their \(k_q\) values were greater than the known rate constant for biradical formation.

Ng and Guillet proposed that energy transfer occurs by a nonclassical mechanism in which peroxide and excited ketone form an encounter complex. Deactivation of the excited ketone occurs via coupling of carbonyl electronic energy and peroxide vibrational energy. The vibrationally excited peroxide then undergoes oxygen-oxygen bond breakage. To rationalize their observation that tert-butyl hydroperoxide gave a \(k_q\) seven times faster than that of DTBP with PS-PVK, Ng and Guillet invoked a steric effect for hydrogen vs. a tert-butyl group. However, since tert-butyl hydroperoxide possesses an abstractable hydrogen atom and DTBP does not, different quenching mechanisms are likely for the two compounds, and the difference in \(k_q\)
is probably not due to steric effects.

In 1978, Koo and Schuster\textsuperscript{25,26} discovered a new thermal reaction of easily oxidized aromatic hydrocarbons with diphenyl peroxyde (DPP). Their proposed mechanism (Scheme III) was called the chemically initiated electron exchange luminescence mechanism (CIEEL) and the aromatic hydrocarbon was termed an activator (ACT). The oxidation potential of the activator served to predict whether the CIEEL mechanism operated, i.e., a plot of $\log k_2$ vs. $E_{1/2}^{\text{ox}}$ gave a straight line. Rubrene, with an oxidation potential of 0.82 V vs. SCE, was an example of a good activator. The singlet energy, uv spectrum, fluorescence efficiency and lifetime of the activator did not correlate with $\log k_2$.

In 1979, Horn and Schuster\textsuperscript{27} reported an important extension of the CIEEL work. The activators were excited states of aromatic hydrocarbons generated by pulsed laser flash photolysis in acetonitrile solvent. Pyrene singlet was an excellent activator, giving a diffusion controlled $k_2$ with DPP ($1.67 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$). An absorption spectrum corresponding to pyrene radical cation was obtained 200 nsec after laser excitation. Anthracene triplet, another good activator, gave a $k_2$ which was not quite diffusion controlled. (See Table I).

Two years later, Zupancic, Horn, and Schuster\textsuperscript{28} showed by laser flash photolysis with nitrogen purged solutions that phthaloyl peroxyde (PP) quenched the triplet states of anthracene and 9-acetylanthracene by the electron transfer mechanism, forming observable sensitizer radical cation intermediates in acetonitrile.

In 1982, Horn and Schuster reported $k_q$ values for DPP and three
Scheme III

\[
\text{DPP} + \text{ACT} \xrightleftharpoons[k_2]{k_{-2}} \text{DPP}^* \text{ACT}^*
\]

\[
\text{DPP}^* \text{ACT}^* \xrightarrow{\text{FAST}} \text{ACT}^+
\]

\[
\xrightarrow{\text{DIFFUSION}} \xrightarrow{\text{NO} \ \text{hv}} \text{ACT}^+
\]

\[
\xrightarrow{-\text{CO}_2} \xrightarrow{\text{CHARGE ANNIHILATION}} \xrightarrow{\text{CHEMILUMINESCENCE}}
\]

\[
\text{OH} \quad \text{OH}
\]

\[
\text{ACT}^* \quad \text{ACT}^+
\]
additional triplet state CIEEL activators, 9-acetylanthracene, 9,10-dibromoanthracene, and fluoranthene.\textsuperscript{29} (See Table I).

In 1981, while the present work with dialkyl peroxides was in progress, Scaiano and Wubbels\textsuperscript{30} reported an extensive laser flash photolysis study of the quenching of aromatic hydrocarbon and aromatic ketone triplets by DTBP in benzene. This technique allowed the direct measurement of triplet \( k_q \) values and revealed a correlation between \( k_q \) and \( E_T \). DTBP was a rather poor quencher and gave \( k_q \) values that were far from diffusion controlled. (See Table I). An electron transfer mechanism was ruled out for this peroxide because the observed rate constants did not correlate with the oxidation potentials of the sensitizers. Also no large increases in rate were observed when the solvent was changed from benzene to the much more polar acetonitrile. An electron transfer process should be favored in acetonitrile because it is better able to solvate charged species. Scaiano and Wubbels proposed a general model for vertical energy transfer to a dissociative excited state, such as the one known\textsuperscript{31} for peroxides. By determining quenching rate constants at different temperatures, Scaiano and Wubbels showed that quenching is an activated process. Their model explained the need for an activation energy but did not specifically consider their unusually low slope of \(-0.072\) for the \( \log k_q \) vs. triplet energy line nor were any predictions made as to the magnitude of this slope for other peroxides. As mentioned earlier, energy transfer normally exhibits a slope of \(-0.733\).

A summary of all the known rate constants for quenching of triplet sensitizers by peroxides is presented in Table I.
<table>
<thead>
<tr>
<th>Peroxide&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Sensitizer</th>
<th>( k_\text{q} )</th>
<th>Method&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Solvent&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
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<td>DTBP</td>
<td>propiophenone</td>
<td>9.6 \times 10^6</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>p-methoxypropiophenone</td>
<td>7.9 \times 10^6</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>benzophenone</td>
<td>3.4 \times 10^6</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>benzophenone</td>
<td>3.7 \times 10^6</td>
<td>LFP</td>
<td>A</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>phenanthrene</td>
<td>1.8 \times 10^6</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>phenanthrene</td>
<td>3.0 \times 10^6</td>
<td>LFP</td>
<td>A</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>naphthalene</td>
<td>1.1 \times 10^6</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>benzil</td>
<td>2.8 \times 10^5</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>fluorenone</td>
<td>2.4 \times 10^5</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>benz[a]anthracene</td>
<td>7.0 \times 10^4</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>DTBP</td>
<td>anthracene</td>
<td>9.7 \times 10^4</td>
<td>LFP</td>
<td>B</td>
<td>30</td>
</tr>
<tr>
<td>BP</td>
<td>benzophenone</td>
<td>3.2 \times 10^6</td>
<td>SV</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>DTBP</td>
<td>PS-PVK&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1.7 \times 10^8</td>
<td>SV</td>
<td>B</td>
<td>24</td>
</tr>
<tr>
<td>DTBP</td>
<td>PS-MIK&lt;sup&gt;h&lt;/sup&gt;</td>
<td>(27.8)&lt;sup&gt;h&lt;/sup&gt;</td>
<td>SV</td>
<td>B</td>
<td>24</td>
</tr>
<tr>
<td>BP</td>
<td>benzophenone</td>
<td>1.4 \times 10^6</td>
<td>SV</td>
<td>B</td>
<td>5</td>
</tr>
<tr>
<td>BP</td>
<td>2-acetonaphthione</td>
<td>8.5 \times 10^4</td>
<td>SV</td>
<td>B</td>
<td>5</td>
</tr>
<tr>
<td>DPP</td>
<td>anthracene</td>
<td>1.4 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>27</td>
</tr>
<tr>
<td>DPP</td>
<td>9-acetylanthracene</td>
<td>2.7 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>29</td>
</tr>
<tr>
<td>DPP</td>
<td>9,10-dibromoanthracene</td>
<td>3.3 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>29</td>
</tr>
<tr>
<td>DPP</td>
<td>fluoranthene</td>
<td>1.9 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>29</td>
</tr>
<tr>
<td>PP</td>
<td>anthracene</td>
<td>7.5 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>28</td>
</tr>
<tr>
<td>PP</td>
<td>9-acetylanthracene</td>
<td>7.3 \times 10^8</td>
<td>LFP</td>
<td>A</td>
<td>28</td>
</tr>
<tr>
<td>AP</td>
<td>benzophenone</td>
<td>9.8 \times 10^8</td>
<td>SV</td>
<td>H</td>
<td>11</td>
</tr>
<tr>
<td>AP</td>
<td>anthraquinone</td>
<td>(45)&lt;sup&gt;i&lt;/sup&gt;</td>
<td>SV</td>
<td>H</td>
<td>11</td>
</tr>
</tbody>
</table>

<sup>a</sup> AP = acetyl peroxide; DTBP = di-tert-butyl peroxide; PP = phthaloyl peroxide; DPP = diphenoyl peroxide; BP = benzoyl peroxide.

<sup>b</sup> \( M^{-1} \text{ sec}^{-1} \)

<sup>c</sup> LFP = laser flash photolysis.

<sup>d</sup> SV = Stern-Volmer plots and an assumed lifetime.

<sup>e</sup> B = benzene; A = acetonitrile; H = heptane.

<sup>f</sup> Assuming \( \tau = 10 \mu \text{sec} \).

<sup>g</sup> PS-MIK = polystyrene co-methyl isopropyl ketone.

<sup>h</sup> PS-PVK = polystyrene co-phenyl vinyl ketone.

<sup>i</sup> Assuming \( \tau = 1000 \mu \text{sec} \); the maximum lifetime ever obtained in the present work was 190 \( \mu \text{sec} \).

<sup>j</sup> Assuming \( \tau = 60 \text{ nsec} \); \( k_\text{q} \tau \) was 53 M\(^{-1} \).
At the start of our work, three groups\textsuperscript{2,15,16} had obtained contradictory bisacetyl results. Smith's quantum yield studies\textsuperscript{5} had shown the mechanism of sensitized decomposition of BP to be more complicated than just triplet energy transfer. Walling and Gibian\textsuperscript{2} had been confused in their interpretation of the role of $E_T$ in the decomposition of peroxides by the intervention of a singlet process. Clearly, unambiguous triplet quenching data were needed.

As mentioned earlier, flash photolysis allows direct measurement of rate constants for fast processes like triplet quenching. This well established technique\textsuperscript{32} has been used to determine rate constants for the interaction of triplets with nitro compounds,\textsuperscript{34} quinones,\textsuperscript{33} stilbenes,\textsuperscript{34} polymers,\textsuperscript{35,36} 1-phenyl-2-(2-naphthyl)-ethene,\textsuperscript{37} inorganic iron complexes,\textsuperscript{38} amines,\textsuperscript{39} nitroxyl radicals,\textsuperscript{40,41} and hydrocarbons.\textsuperscript{42} An attractive feature of flash photolysis compared to quantum yield experiments is the fact that there is no need to know the exact chemistry which follows quenching. Also, quantum yield methods require prior knowledge of the lifetime of the triplet in order to calculate $k_q$. For triplets in solution, lifetimes are sensitive to purity of solvents and vary from lab to lab and from experiment to experiment. Lifetimes are measured directly by flash photolysis.

The advent of lasers has made flash photolysis even better by allowing the measurement of nanosecond lifetimes instead of the microsecond lifetimes available by older methods. When one is dealing with microsecond lifetimes, the laser decays during the very early part of transient absorption so that it does not interfere with analysis of the data. Furthermore, the monochromatic nature of the laser beam
allows selective excitation of sensitizers without concommitant irradiation of quenchers. Also, a laser can be rapidly pulsed, allowing the summing of data from many pulses thus greatly enhancing the signal to noise ratio of decay curve data. The combination of a pulsed laser and a transient digitizer gives the additional advantages of rapid data acquisition and easy computer analysis. These techniques far surpass the older methods which rely on oscilloscopes, cameras, and chart recorders.

A major part of this thesis project was construction of a laser flash photolysis facility. This instrumentation was then used to measure $k_q$ for a series of triplet sensitizers and alkyl peroxides. At the outset, we sought to answer the following questions about alkyl peroxides: 1.) How do $k_q$ values depend on peroxide structure? 2.) How do $k_q$ values depend on $E_T$? 3.) Are $k_q$ values influenced by steric effects?

As recent literature reports in this active field appeared, we became interested in two additional questions about alkyl peroxides: 1.) Is an electron transfer quenching mechanism important? 2.) Is the slope of the log $k_q$ vs. $E_T$ line always as low as Scaiano's value $^{30}$ regardless of peroxide?
RESULTS

Quenching rate constants were obtained for six alkyl peroxides whose structures, names, and abbreviations are shown below.

\[
\begin{align*}
\text{di-2-phenylethyl peroxide} & \quad 2,3\text{-dioxabicyclo[2.2.1]heptane} \\
\text{ascaridole} & \quad \text{dihydroascaridole} \\
\text{ASC} & \quad \text{DHASC} \\
\text{3,3,6,6-tetramethyl-1,2-dioxacyclohexane} & \quad \text{di-tert-butyl peroxide} \\
\text{TDC} & \quad \text{DTBP}
\end{align*}
\]
A block diagram of the laser flash photolysis apparatus is shown in Figure 1. Sensitizer triplet states were created by 337 or 351 nm laser light pulses incident on degassed or nitrogen purged solutions. The $T_{1}-T_{2}$ absorbance was monitored with a steady state xenon or tungsten lamp perpendicular to the laser beam. The intensity profile of the analyzing light reaching a photomultiplier over a given period of time was frozen with a transient digitizer and the data were plotted on a graphics terminal. Figure 2 shows typical decay curve data for 10 laser shots.

Decay of sensitizer triplets was monitored at literature maxima for $T_{1}-T_{2}$ absorption. Toward the middle of this study, we were able to obtain our own spectra. Figure 3 shows the $T_{1}-T_{2}$ spectrum of 2-acetonaphthone, which matches the one reported in the literature.43

First order computer analysis of the data gave triplet lifetimes at various peroxyde concentrations. These were analyzed by the Stern-Volmer equation44 to yield $k_{q}$:

$$\frac{1}{\tau} = \frac{1}{\tau_{0}} + k_{q}[Q]$$

$\tau = \text{lifetime with quencher}$

$\tau_{0} = \text{lifetime with no added quencher}$

$[Q] = \text{quencher concentration in mol liter}^{-1}$

At high concentration, triplets undergo $T-T$ annihilation, which introduces a second order component into the decay curves. We therefore ignored the early portion of the decay curves when analyzing
Figure 1. Block diagram of laser flash photolysis apparatus.
Figure 2. Typical decay curve of $T_1-T_2$ absorption following laser excitation.
Figure 3. $T_1 - T_2$ absorption spectrum of 2-acetonaphthone.
our data because this part is most distorted by second order decay. The mixed first and second order data analysis of Linschitz and Sarkasen\(^\text{45}\) was applied in some cases and gave rate constants close to those obtained by the above truncation method. Since the truncation method is much simpler, it was generally used. Occasionally, screens were inserted between the laser and the sample cell to attenuate the laser beam intensity and the amount of second order decay.

Table II lists the \(k_q\) values obtained in benzene solution. Except as noted, at least four and often six peroxyde concentrations were used to obtain each \(k_q\) value. The Stern-Volmer plots are shown in Appendix A.

Figures 4-8 show plots of \(E_m\) vs. \(\log k_q\) for each peroxyde. Although there is some scatter, the amount is not unusual for this kind of work. Our correlation coefficients are higher than those of Sandros\(^\text{7}\) (0.856) or of Scaiano and Wubbels\(^\text{30}\) (0.911). Table III shows the slopes of these plots.

Table IV lists the \(k_q\) values obtained for ascaridole in acetonitrile.

In addition, we obtained a few rate constants for BP and tert-butylerbenzoate (TBPB) which are shown in Table V. The \(E_m\) vs. \(\log k_q\) plot for TBPB is shown in Figure 9.
Table II

Quenching Rate Constants\(^a\) in Benzene Solution

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>(E_T^b)</th>
<th>PEP</th>
<th>DTBP(^c)</th>
<th>TDC</th>
<th>ASC</th>
<th>DHASC</th>
<th>221(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p)-methoxyacetophenone</td>
<td>71.5</td>
<td>27</td>
<td>0.58</td>
<td>0.38(^e)</td>
<td>70</td>
<td>57</td>
<td>190</td>
</tr>
<tr>
<td>triphenylene</td>
<td>66.6</td>
<td>12</td>
<td>0.26((1.01))</td>
<td>0.65(^f)</td>
<td>52</td>
<td>-</td>
<td>210</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>65.5</td>
<td>25</td>
<td>0.22</td>
<td>-</td>
<td>64</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>59.3</td>
<td>1.7</td>
<td>0.077((0.032))</td>
<td>0.031</td>
<td>4.8</td>
<td>7.9</td>
<td>278(^e)</td>
</tr>
<tr>
<td>biacetyl(^h)</td>
<td>55</td>
<td>-</td>
<td>0.038((0.014))</td>
<td>&lt;0.0027(^g)</td>
<td>1.0(^g)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>53.3</td>
<td>0.13(^i)</td>
<td>0.024</td>
<td>0.0016(^g)</td>
<td>1.6</td>
<td>0.91</td>
<td>10</td>
</tr>
<tr>
<td>pyrene</td>
<td>48.2</td>
<td>-</td>
<td>0.012</td>
<td>-</td>
<td>0.7(^g)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>acridine</td>
<td>45.3</td>
<td>0.012(^i,(^g)</td>
<td>0.0075</td>
<td>-</td>
<td>0.069</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>anthracene</td>
<td>42.6</td>
<td>0.25(^i,(^g)</td>
<td>0.0097</td>
<td>-</td>
<td>0.016(^g)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(a\) \(x 10^{-7}\) M\(^{-1}\) sec\(^{-1}\)  
\(b\) Triplet energy (kcal mol\(^{-1}\)).  
\(c\) Calculated using the reported slope and a point on the \(E_T\) vs. log \(k\) line from reference 30 except for 9-fluorenone and anthracene for which reference 30 experimental values are shown. Values in parentheses are experimental values from this work.  
\(d\) Data obtained with one laser flash.  
\(e\) Mixed order data analysis.  
\(f\) Determined by Dr. Matthew A. Page in 1979.  
\(g\) Two peroxide concentrations only.  
\(h\) Determined by lifetime of phosphorescence emission.  
\(i\) Total final absorbance unequal to sum of components.
Figure 4.

Figure 5.
Figure 6. 

Figure 7.
Figure 8.

Figure 9.
Table III

Log $k_q$ vs. $E_T$ First Order Fit Parameters

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>Slope$^a$</th>
<th>Std. dev.$^b$</th>
<th>Correl. coef.$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEP</td>
<td>0.139</td>
<td>0.014</td>
<td>0.980</td>
</tr>
<tr>
<td>DTBP$^d$</td>
<td>0.074</td>
<td>0.013</td>
<td>0.911</td>
</tr>
<tr>
<td>TDC</td>
<td>0.146</td>
<td>0.028</td>
<td>0.948</td>
</tr>
<tr>
<td>ASC</td>
<td>0.125</td>
<td>0.012</td>
<td>0.969</td>
</tr>
<tr>
<td>DHASC</td>
<td>0.095</td>
<td>0.021</td>
<td>0.976</td>
</tr>
<tr>
<td>221$^e$</td>
<td>0.115</td>
<td>0.026</td>
<td>0.976</td>
</tr>
</tbody>
</table>

$^a$ mol kcal$^{-1}$
$^b$ Standard deviation of the slope.
$^c$ Correlation coefficient.
$^d$ Our calculation from data in reference 30.
Actual reference 30 slope is 0.072.
$^e$ The slope was calculated from the thioxanthone, 2-acetonaphthone, and 9-fluorenone data only. Quenching was possibly diffusion controlled with sensitizers of higher triplet energy than these.
Table IV

Ascaridole Quenching Rate Constants in Acetonitrile Solvent

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$k_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxyacetophenone</td>
<td>33</td>
</tr>
<tr>
<td>triphenylene</td>
<td>11</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>4.5</td>
</tr>
<tr>
<td>acridine</td>
<td>b</td>
</tr>
</tbody>
</table>

$a \times 10^{-7} \text{ M}^{-1} \text{sec}^{-1}$

$b$ Sporadic lifetimes were obtained with nitrogen purged sensitizer only solutions. Ground state chemistry was suspected. However, no change in the normal ground state uv spectrum occurred after 1000 laser shots in a separate experiment.

Table V

Quenching Rate Constants $^a$ for Acyl Peroxides in Benzene Solvent

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>TBPB</th>
<th>BP$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxyacetophenone</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>triphenylene</td>
<td>-</td>
<td>16</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>0.086</td>
<td>0.20</td>
</tr>
<tr>
<td>bisacetyl</td>
<td>-</td>
<td>0.0071</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>0.0056</td>
<td>-</td>
</tr>
<tr>
<td>acridine</td>
<td>-</td>
<td>0.054</td>
</tr>
</tbody>
</table>

$a \times 10^{-7} \text{ M}^{-1} \text{sec}^{-1}$

$b$ Two data points only.
Figures 4–8 show that for any given peroxide, quenching rate constants decrease as sensitzer triplet energy decreases. The slopes of the $\log k_q$ vs. $E_T$ plots which are shown in Table III are about the same for all six peroxides and are higher than the literature slope for DTBP.\textsuperscript{30} Our DTBP data give a slope based on three points of $0.164 \pm 0.033$, which is also higher than the reported\textsuperscript{30} value.

With the exception of TDC, all the peroxides studied are better quenchers than DTBP though none of them give diffusion controlled quenching\textsuperscript{46} ($1.0 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$). For p-methoxyacetophenone as sensitizer, the rate constants decrease in the order 221 > ASC > DHASC > PEP > DTBP > TDC.

221 is the best quencher and is also the most unstable peroxide. We therefore decided to look for a correlation between $k_q$ and peroxide thermolysis activation parameters (Table VI). Figures 10–12 show plots of $\Delta G^+$ vs. $\log k_q$ for the three sensitizers for which we have the most complete data. The three plots have the same shape and the correlation coefficients are $> 0.85$. Similar plots for $\Delta H^+$ were much more scattered. Thus, thermal lability is an important factor, though not the only one, governing triplet quenching rate constants.

An exchange triplet energy transfer mechanism best explains our results, in agreement with the conclusions of Scaiano and Wubbels.\textsuperscript{30} A diagram illustrating their model for energy transfer to compounds with dissociative excited states is shown in Figure 13. Low slopes mean that low energy sensitizers are more efficient than predicted by the
classical model. The distance BC is shorter for peroxides than for substances with bound triplet states. Peroxides can undergo vertical excitation at BC if the energy required to go from point O to point C is made up by the thermal energy of the peroxide ground state.

Table VII shows the ratio of $k_q$ for several peroxides to the $k_q$ for DTBP. The quenching rate constants for DTBP could be low due to a steric effect, a possibility also considered by Scaiano and Wubbels. For example, PEP is a 50 fold better quencher of p-methoxyacetophenone than DTBP. Wamser observed a factor of 3-12 for azo-tert-butane relative to azo-n-butane. Steric effects for peroxides are probably similar to those for azo compounds due to the similar size of the two types of compounds. The oxygen van der Waals radius is 0.1 Å smaller than the nitrogen atomic radius while the oxygen-oxygen single bond length of 1.475 Å for peroxides is longer than the nitrogen-nitrogen double bond length of 1.254 Å for azo compounds. It is doubtful that steric effects account for all the increase in rate for DHASC or 221 relative to DTBP because Wamser observed factors of only 4.8 and 11 for the analogous azo compounds.

The possibility of quenching by the electron transfer mechanism shown below was considered.

$$\text{sensitizer}^{3} + \text{peroxide} \rightarrow \text{sensitizer}^{*} + \text{peroxide}^{2}$$

Unfortunately, the ketone sensitizers which we studied are of unknown oxidation potential; hence, plots of log $k_q$ vs. oxidation potential cannot be constructed. However, the fact that our quenching rate constants for ASC in benzene and acetonitrile show no rate enhancement in the more polar solvent argues against electron transfer. Scaiano
and Wubbels\textsuperscript{30} also found no solvent effect for DTBP. Schuster and Koo\textsuperscript{25} observed a solvent effect of 5 for acetonitrile versus benzene for the DPP-perylene CIEEL system. Kuzmin et. al.\textsuperscript{33} observed a solvent effect of 4.5 for acetonitrile versus benzene for the 1,2-benzanthrene triplet p-bromonitrobenzene electron transfer system. Acyl peroxides are easier to reduce than dialkyl peroxides\textsuperscript{51} which may explain why Schuster observes electron transfer quenching and we do not.
Table VI

Peroxide Thermolysis Activation Parameters

<table>
<thead>
<tr>
<th>Peroxide</th>
<th>$\Delta H^+$</th>
<th>$\Delta S^+$ e.u.</th>
<th>$\Delta G^{+#}(298^\circ)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEP</td>
<td>33.3</td>
<td>3.5</td>
<td>32.2</td>
<td>b</td>
</tr>
<tr>
<td>TDC</td>
<td>32</td>
<td>-13</td>
<td>36</td>
<td>52</td>
</tr>
<tr>
<td>ASC</td>
<td>30.6</td>
<td>2.2</td>
<td>29.9</td>
<td>53</td>
</tr>
<tr>
<td>DHASC</td>
<td>33.1</td>
<td>3</td>
<td>32.2</td>
<td>c</td>
</tr>
<tr>
<td>221</td>
<td>20.7</td>
<td>-19</td>
<td>26.4</td>
<td>54</td>
</tr>
<tr>
<td>DTBP</td>
<td>36.6</td>
<td>10.3</td>
<td>33.5</td>
<td>55</td>
</tr>
</tbody>
</table>

$^a$ kcal mol$^{-1}$

$^b$ Determined by DSC in this work.

$^c$ Value for 2,3-dioxabicyclo[2.2.2]octane in reference 54. — DSC in this work gave $\Delta H^+ = 34.6$ kcal mol$^{-1}$, $\Delta S^+ = 0.22$ e.u., and $\Delta G^{+\#} = 34.6$ kcal mol$^{-1}$.

$^d$ See the experimental section for the DSC traces and data analyses. Midrange temperatures of 167 ºC for PEP and 220 ºC for DHASC were used to calculate $\Delta H^+$ and $\Delta S^+$.

Table VII

Quenching Rate Constants Relative to DTBP

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>DTBP</th>
<th>PEP</th>
<th>TDC</th>
<th>ASC</th>
<th>DHASC</th>
<th>221</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxyacetophenone</td>
<td>(1)$^a$</td>
<td>46</td>
<td>0.66</td>
<td>121</td>
<td>98</td>
<td>328</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>(1)$^b$</td>
<td>22</td>
<td>0.41</td>
<td>62</td>
<td>103</td>
<td>351</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>(1)$^b$</td>
<td>5.4</td>
<td>0.07</td>
<td>67</td>
<td>38</td>
<td>417</td>
</tr>
</tbody>
</table>

$^a$ $k_q$ calculated from data in reference 30.

$^b$ $k_q$ from reference 30.
Figure 10.
Figure 13. Model for energy transfer to dissociative excited state from Ref. 30.
EXPERIMENTAL

General Lab Equipment

Nuclear magnetic resonance spectra were obtained on a Varian EM-390 or JEOL FX-90Q spectrometer using TMS as reference. Ultraviolet spectra were obtained on a Cary 17 spectrometer. Gas Chromatography was done on an ANTEK Model 340 instrument. Phosphorescence and fluorescence spectra were obtained on a Perkin-Elmer MPF-2A fluorescence spectrophotometer. The mass spectrum was obtained on a Finnigan 3300 GC-MS system. Differential scanning calorimetry was done on a Mettler TA 3000 DSC. Melting points were obtained from a Laboratory Devices Mel-Temp apparatus and are uncorrected. An ISCO Model 2111 Fraction Collector was used for column chromatography.

Solvents

Benzene (Fisher Certified Reagent, Thiophene free) was purified by the method of Hammond and Herkstroeter. A three liter batch containing 2-3 g of o-chloranil was irradiated with a Hanovia medium pressure lamp for at least 10 days with stirring under nitrogen. Additional chloranil (1-2g) was added after one week and the sides of the irradiation well were scraped free of brown side products. Then the benzene was passed through a 76 cm x 3 cm o.d. column of alumina (Alcoa F-20) which had been activated by heating (50-100 °C, 1-10 mm, one hour) and stored under vacuum. This "flash benzene" was distilled under nitrogen from P2O5 as needed.

Acetonitrile was purified by the method of O'Donnell, Ayres, and Mann. Baker reagent grade acetonitrile (800 ml) was distilled from
sodium carbonate (10 g) and potassium permanganate (15 g). The
distillate (700 ml) was acidified (10–12 drops conc. sulfuric acid),
filtered to remove the white ppt that formed, and redistilled through a
7 in. column packed with glass helices, collecting the middle fraction
(500 ml). The 10% transmittance uv cutoff (acetonitrile vs. deionized
water) was improved by the above treatment from 232 nm to 227 nm and an
impurity broadly absorbing at 260–335 nm was removed. Simple
distillation of reagent grade acetonitrile from calcium hydride caused
no improvement in the 10% uv cutoff.

Isopropanol (Mallinckrodt, Analytical Reagent) was distilled from
calcium oxide.

Methylene chloride and pentane were distilled from calcium
hydride.

Sensitizers

Triphenylene, thioxanthone, 9-fluorenone, and acridine came from
a laboratory collection of sensitizers purified by either
recrystallization or zone refining. Uv spectra were compared with
literature uv spectra before use.

Biacetyl was dried over magnesium sulfate then carefully
fractionally distilled under nitrogen through a 60 cm x 1 cm i.d.
silvered column packed with glass helices. Small aliquots (1–2 g) of
the middle fraction were sealed into 10 cm x 7 mm ampules after
degassing by two freeze pump thaw cycles on the vacuum line (10⁻⁴ mm).
Ampules were stored in the refrigerator and a fresh ampule was used for
each experiment.

p-Methoxyacetophenone was vacuum distilled,⁵⁷ recrystallized from
ether-petroleum ether, then pumped on to remove traces of solvent (10 mm, room temperature, 20 min.). White crystals resulted (mp 34-36 °C, lit 38-39 °C).

2-Acetonaphthone was recrystallized twice from absolute reagent methanol and twice from hexane. White crystals resulted (mp 53.8-54.8 °C, lit 56°C).

Pyrene was zone refined by Mr. Douglas W. Horsey in this laboratory.

Anthracene was zone refined by Dr. A. R. McGhie at the University of Pennsylvania.

The uv and photophysical properties of the sensitizers used in this study are shown in Tables VII and IX.

**General Comments About Peroxide Handling**

Peroxides can be shock sensitive or can decompose violently upon heating. General references to their safe handling are provided.\(^5^{8-60}\)

Active Oxygen Content (AOC) is defined as \((16/M) \times 100\) where \(M\) is the molecular weight of the peroxide. A general rule of thumb states that relatively "safe" peroxides have an AOC under 5\(^%\).\(^6^{1}\)

In this lab the following precautions were taken when handling peroxides: 1.) Work was done on a 1-2 g scale; 2.) Safety goggles and safety shields were used; 3.) Solvents were rotovapped from new peroxides after taping the flasks containing them with electrical tape; 4.) Distillation was avoided. When distillation was necessary, the lowest possible temperatures were used.

**Peroxides**

Di-tert-butyl peroxyde (Lucidol) was freed of hydroperoxide by
Table VIII

Sensitizer UV and Lifetime Properties

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$\varepsilon_{337}$</th>
<th>$\varepsilon_{351}$</th>
<th>$\lambda_{\text{max}}$ $^a$</th>
<th>$\tau_{\text{lit}}$ $^b$</th>
<th>Typical purge $\tau$ $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxyacetophenone</td>
<td>73</td>
<td>25</td>
<td>405$^c$</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>triphenylene</td>
<td>331</td>
<td>17</td>
<td>428</td>
<td>625</td>
<td>65</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>980</td>
<td>-</td>
<td>610$^c$</td>
<td>77</td>
<td>15</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>1250</td>
<td>509</td>
<td>435</td>
<td>333</td>
<td>48</td>
</tr>
<tr>
<td>biacetyl</td>
<td>2.2</td>
<td>3.3</td>
<td>330</td>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>131</td>
<td>166</td>
<td>435</td>
<td>333</td>
<td>47</td>
</tr>
<tr>
<td>pyrene</td>
<td>3860</td>
<td>798</td>
<td>420</td>
<td>1540</td>
<td>300</td>
</tr>
<tr>
<td>acridine</td>
<td>4970</td>
<td>5980</td>
<td>440$^c$</td>
<td>400</td>
<td>28</td>
</tr>
<tr>
<td>anthracene</td>
<td>3560</td>
<td>2960</td>
<td>420</td>
<td>370</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Used in this work. Useful general references are provided in reference 62.

$^b$ Reference 34 for all but biacetyl. Biacetyl: Reference 22.

$^c$ Determined experimentally in this work.
Table IX

Sensitizer Photophysical Properties

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>$E_T^n$</th>
<th>Lowest triplet configuration</th>
<th>$\Phi_{isc}^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxyacetophenone</td>
<td>71.5</td>
<td>$n, \pi^*$</td>
<td>-</td>
</tr>
<tr>
<td>triphenylene</td>
<td>66.6</td>
<td>$\pi, \pi^*$</td>
<td>0.95</td>
</tr>
<tr>
<td>thioxanthone</td>
<td>65.5</td>
<td>$\pi, \pi^*$</td>
<td>1.00</td>
</tr>
<tr>
<td>2-acetonaphthone</td>
<td>59.3</td>
<td>$\pi, \pi^*$</td>
<td>0.84</td>
</tr>
<tr>
<td>biacetyl</td>
<td>55</td>
<td>$n, \pi^*$</td>
<td>0.98</td>
</tr>
<tr>
<td>9-fluorenone</td>
<td>53.3</td>
<td>$n, \pi^*$</td>
<td>0.93</td>
</tr>
<tr>
<td>pyrene</td>
<td>48.2</td>
<td>$\pi, \pi^*$</td>
<td>0.08</td>
</tr>
<tr>
<td>acridine</td>
<td>45.3</td>
<td>$\pi, \pi^*$</td>
<td>0.76</td>
</tr>
<tr>
<td>anthracene</td>
<td>42.6</td>
<td>$\pi, \pi^*$</td>
<td>0.75</td>
</tr>
</tbody>
</table>

a Reference 63.
passage neat through Woelm Alumina that had been activated by heating (one hour, 130 °C, 5mm). Pasteur pipettes (5 3/4 in.) made convenient columns. Bulb to bulb distillation (room temperature, 6mm) afforded pure DTBP.

Ascaridole (K and K Laboratories, Inc.) was low temperature recrystallized at -78 °C three or four times from dry 2-methylbutane or dry pentane (1-2 g in 10-12 ml solvent). The white crystals that formed melted to a pale yellow liquid by the time room temperature was reached (1lt mp 3.3 °C). The compound was further purified by molecular distillation (oil bath temperature 65 °C, 0.75 mm). CAUTION: Ascaridole explodes upon heating at 1 atm.

3,3,6,6-Tetramethyl-1,2-dioxacyclopentane was synthesized by Dr. Matthew A. Page by the method of Criegee. The purity was checked by nmr. The peroxide was still pure after four years of refrigerator storage.

tert-Butylperbenzoate (Lucidol) was checked by TLC on silica gel with methylene chloride as solvent. Uv and Fe(II) visualization showed the presence of a peroxodic impurity (probably tert-butyl hydroperoxide) and a uv impurity. Passage of neat peroxide through basic alumina removed both impurities. The NMR: \( \text{CDCl}_3 \) \( \delta \) 1.40 (9 H, s), 7.28-8.04 (5 H, m) matched the literature nmr.

Benzoyl peroxide was recrystallized before use. Peroxide (4g) was dissolved in reagent grade chloroform at room temperature and the resulting solution was filtered. Anhydrous reagent methanol (18 ml) was added to the filtrate. Refrigeration of the solution afforded white crystals (1.7 g, no mp attempted).
The UV properties of the peroxides used in this study are shown in Table X.

**Peroxide Thin Layer Chromatography**

Fe(II) visualizing reagent. 68 Ferrous ammonium sulfate $6\text{H}_2\text{O}$ (1.2 g), water (12.5 ml), concentrated sulfuric acid (4 drops), and ammonium thiocyanate (0.625 g) were mixed together in the order listed. Peroxides such as PEP, 221, DHASC, and tert-butylperbenzoate gave a red color with this reagent. The strength of the color seems to follow the order $\text{H}_2\text{O}_2 \rightarrow \text{ROOH} \rightarrow \text{ROOR}$. The red solution turns rust brown with age and must be made fresh daily. A sprayer is not essential for application to TLC plates. Satisfactory results were obtained when drops of reagent were placed directly on the plate with a Pasteur pipette.

**Spot Test I.** A small TLC plate was spotted with the solution to be tested for peroxide followed by a drop of Fe(II) visualizing agent and the color was noted.

**TLC.** Fe(II) visualization is destructive. Uv visualization, if desired, must be done first. If iodine and uv visualization are both desired, a TLC plate must be spotted twice, eluted, then cut apart and each half visualized separately first with uv light then one half with iodine and the other half with Fe(II) reagent.

**Low Temperature TLC.** The elution jar was placed in a low temp bath and TLC run as usual.

**Synthesis and Purification of Compounds**

**Synthesis of 2-phenylethyl mesylate.** The mesylate was prepared from the alcohol by the method of Crossland and Servis 69. A 1000 ml
<table>
<thead>
<tr>
<th>Peroxide</th>
<th>$\varepsilon_\text{337}^a$</th>
<th>$\varepsilon_\text{351}^a$</th>
<th>Density$^b$</th>
<th>Mol wt$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASC</td>
<td>2</td>
<td>1.15</td>
<td>1.013</td>
<td>168</td>
</tr>
<tr>
<td>DHASC</td>
<td>2.3</td>
<td>1.41</td>
<td>0.908</td>
<td>170</td>
</tr>
<tr>
<td>PEP</td>
<td>2.2</td>
<td>1.01</td>
<td>1.04</td>
<td>242</td>
</tr>
<tr>
<td>TDC</td>
<td>0.5</td>
<td>d</td>
<td>0.902</td>
<td>144</td>
</tr>
<tr>
<td>DTBP</td>
<td>0.49</td>
<td>0.1</td>
<td>0.794</td>
<td>146</td>
</tr>
<tr>
<td>221</td>
<td>7</td>
<td>3</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>TBPB</td>
<td>0.25</td>
<td>0.12</td>
<td>1.03</td>
<td>194</td>
</tr>
<tr>
<td>BP</td>
<td>10</td>
<td>$&lt;10$</td>
<td>-</td>
<td>242</td>
</tr>
</tbody>
</table>

a $\text{M}^{-1}\text{cm}^{-1}$  
b $\text{g mL}^{-1}$  
c $\text{g mol}^{-1}$  
d 0 at 0.107 M
3NRB flask equipped with a mechanical overhead stirrer, addition funnel, nitrogen inlet, and a low temperature thermometer was charged with 2-phenylethyl alcohol (Aldrich, 12 g, 0.1 mole), dry methylene chloride (400 ml), and triethylamine which was freshly distilled from calcium hydride. Methanesulfonyl chloride (Aldrich, 8.47 ml, 0.11 mole) dissolved in methylene chloride (25 ml) was added dropwise over a period of 20–30 min. to the ice-cooled flask such that the temperature remained at 10–12 °C. The reaction was stirred 30 min. more. A white solid which separated out was redissolved with more solvent (200 ml). The product was worked up by washing the methylene chloride solution twice with 100 ml portions of ice water, once with 100 ml of cold 10% HCl, once with 100 ml sat. sodium bicarbonate and once with 100 ml sat. sodium chloride solution. The final methylene chloride layer was dried over anhyd. potassium carbonate and filtered. The solvent was removed by rotovap leaving a pale yellow, irritating liquid (20.17 g, 100% yield). The NMR: (CDCl₃) 8 7.28 (5 H, s), 4.44 (2 H, t), 3.06 (2 H, t), 2.84 (3 H, s) matched the literature spectrum⁷⁰. PEP was prepared from this compound without further purification.

Synthesis of di-2-phenylethyl peroxide (PEP). The peroxide was prepared from the mesylate and hydrogen peroxide in base by the method of Welch, Williams, and Mosher⁷¹ for dialkyl peroxides. The following example was the largest scale reaction attempted.

The 30% hydrogen peroxide solution used was found to be actually 25% by the titration of Wagner, Smith, and Peters⁷².

A 250 ml 3NRB flask equipped with a low temperature thermometer, addition funnel, and a magnetic stirring bar was charged with
2-phenylethyl mesylate (10.0 g, 0.05 mole), reagent methanol (32 ml), and 25% hydrogen peroxide (3.4 g, 0.025 mole) and was then cooled in ice. A 50% by weight aqueous KOH solution (5.6 g, 0.05 mole) was added dropwise over a period of 20 min. such that the temperature remained at 5–10.5 °C. The flask was allowed to warm gradually to room temperature and was then stirred for 17 hours more, resulting in a yellow solution with a white ppt. The progress of the reaction was followed by TLC on silica gel with methylene chloride solvent and uv and Fe(II) visualization. The reaction did not go to completion even with prolonged stirring, or the addition of more KOH or more hydrogen peroxide. The product mixture, which contained at least four components, was worked up by adding water (125 ml) then extracting at least six times with 50 ml portions of methylene chloride. The peroxide content of the methylene chloride extracts was monitored with Spot Test I. The combined extracts were washed three times with 50 ml portions of 5% KOH (to remove any hydroperoxide) and two times with 50 ml portions of water (the final water layer should be neutral) then dried over anhyd. sodium sulfate. The solvent was removed by rotovap leaving a yellow liquid (6.32 g). The peroxide was isolated by column chromatography as follows.

Peroxide product mixture (3 g) was loaded onto a 75 cm x 3 cm o.d. column slurry packed with 115 g silica gel that had been dried in an oven and cooled in a dessicator before use. The column was eluted with 5 vol % ethyl acetate-hexanes, collecting 12–15 ml fractions. (Reagent grade solvents were used without further purification. Batches of 5% ethyl acetate-hexanes were stored over Linde 4A molecular sieve
before use). Fractions were tested for peroxide with Spot Test I. Peroxide was the first eluted substance followed by 2-phenylethylmethyl ether. Fractions giving positive Spot Test I results were TLC'd on silica gel. The ether was visualized by uv. Fractions containing peroxide only were combined and the solvent removed by rotovap. The colorless to pale yellow liquid which remained (0.5-0.7g) was checked for purity by nmr. Ether impurity NMR: (CDCl₃) δ 2.88 (t), 3.36 (s), 3.6 (t), 7.24 (s).

The synthesis and chromatography were repeated until a total of 2.5 g peroxide was obtained. The combined batches were cautiously distilled in the molecular still using the vacuum line (bp 87-90 °C, 0.0025-0.005 mm) and three traps: the normal vacuum line trap, the Toepler pump trap, and an additional trap between the latter trap and the still. The excellent vacuum was needed because DSC indicated that the compound begins to homolyze at 110 °C. NMR: (CDCl₃) δ 7.24 (5 H, s), 4.18 (2 H, t), 2.92 (2 H, t). Mass spectrum: m/e 242. UV: (hexanes) λ (ε M⁻¹ cm⁻¹) 280sh (38), 268 (328), 264 (390), 261 (427), 259 (490), 253 (421), 248 (338), 244 (266). DSC indicated a mp of 3 °C for this compound. All attempts at low temperature recrystallization from pentane or methanol failed.

**Synthesis of dihydroascaridole (DHASC).** Dihydroascaridole was prepared by the catalytic hydrogenation of ascaridole by the method of Paget. Ascaridole (0.6460 g, 3.84 mmole) was weighed into a 10 ml SNRB flask. Absolute ethanol (6 ml), a magnetic stirring bar, and Adams PtO₂ catalyst (approx. 2 mg) were added. The flask was connected to a 1 atm hydrogenation apparatus and the solution was cooled to -78°C. The
apparatus was evacuated, flushed with hydrogen, and filled with hydrogen. [IMPORTANT: Cooling to -78 °C was necessary to prevent excessive uptake of hydrogen during the evacuation, flushing, and filling processes and subsequent homolysis of the O=O bond. The catalyst was activated within seconds during the flushing operation on a previous experiment at 0 °C.] The cooling bath was removed and the catalyst changed color from brown to its active black state in about 5-10 min. Hydrogen (93.3 ml, 3.84 mmole) was taken up in a period of 70 minutes. The reaction flask was cooled again while the apparatus was evacuated. After warming to room temperature, the reaction was worked up by adding 3-4 ml more absolute ethanol and a spatula of activated charcoal. The solution was suction filtered through a 1/4 in. pad of Celite on a medium porosity fritted filter. The flask was rinsed at least three times with 2-3 ml portions of ethanol and the washings poured through the filter. Solvent was removed from the colorless filtrate by rotovap leaving pale yellow DHASC in quantitative yield. The NMR: (CDCl₃) δ 1.36-2.10 (9 H, m), 1.10 (3 H, s), 0.86 (6 H, d, J = 7 Hz) matched the literature nmr. In addition, a trace of ascaridole and a small amount of an impurity (diol likely) was present. Impurity NMR: δ 0.90 (d).

**Purification of dihydroascaridole.**

A. **Diol removal.** DHASC (0.65 g) was dissolved in 20 ml dry methylene chloride. The solution was passed through two 5 3/4 in. Pasteur pipettes packed with Woelm basic Alumina. Fresh solvent (10 ml) was passed through the columns. Spot Test I on alumina indicated peroxide in the filtrate. Solvent was removed by rotovap leaving DHASC
(0.59 g). The amount of diol present had decreased as shown by nmr.

B. **Low temperature recrystallization.** DHASC (0.59 g) was dissolved in 3 ml dry pentane. The solution was cooled with dry ice and white crystals formed. The cold apparatus was carried to the cold room where the solvent was removed with an aspirator and the crystals were rinsed with a few drops of cold pentane. The apparatus was taken apart, and the crystals removed. The crystals melted to a pale yellow liquid (0.45 g) before reaching room temperature. (lit mp 19.5 °C). A melting curve was not obtained on one DSC attempt where the sample was only cooled to 0 °C. The recrystallized DHASC was then pumped on for 10 min. (room temperature, 19mm). No solvents remained as shown by nmr.

**Synthesis of 2,3-dioxabicyclo[2.2.1]heptene.** This peroxide was prepared by singlet oxygen addition to cyclopentadiene by the method of Adam. 76

Dipotassium azodicarboxylate (KAD) was synthesized from azodicarbonamide by the method of Berson, Poonian, and Libby and stored under vacuum in a dessicator until use.

Cyclopentadiene (1.50 g, 22.7 mmole) was dissolved in 100 ml dry methylene chloride. The solution was dried over anhydrous potassium carbonate, filtered into the photooxygenation apparatus shown in Figure 14, and methylene blue hydrochloride (23 mg) was added. The apparatus was cooled to −78 °C in a windowed dewar while purging the solution with nitrogen and protecting the outlet with a Drierite filled drying tube. After the irradiation set-up shown in Figure 15 was assembled, the nitrogen purge was discontinued, an oxygen purge begun, and irradiation with a 400 W sodium lamp that was vertically mounted with the bulb
Figure 14. Irradiation vessel for singlet oxygen addition.

Figure 15. Top view of the singlet oxygen photoaddition set up.
hanging below the socket was started. While the lamp was turned off, aliquots of the reaction mixture were taken every hour by means of a syringe whose needle was attached to a piece of teflon tubing. The progress of the reaction indicated by the disappearance of cyclopentadiene was followed by GC. A 1/4 in. X 20 ft. TCEP column at 100 °C and TC detection was used. Peaks were observed for air, cyclopentadiene (retention time = 7.8 min. with a 30 ml/min helium carrier gas flow rate), and methylene chloride in that order. No peak was observed for the very unstable peroxide product. Dry ice was added to the dewar frequently during the 90 min. to 200 min. reactions. The product, which is known to decompose violently at 0 °C, was not isolated. The product solution was purged with nitrogen and kept at -78 °C for a short time until the apparatus required in the next step was ready.

**Synthesis of 2,3-dioxabicyclo[2,2,1]heptane (221).** This peroxide was prepared by diimide reduction of 2,3-dioxabicyclo[2,2,1]heptene by the method of Adam. KAD (22.02 g, 0.1135 mole) was placed with 35 ml methylene chloride in a 500 ml nitrogen purged 3NHB flask equipped with an overhead mechanical stirrer, Claisen adapter, low temp thermometer, nitrogen inlet, low temperature addition funnel charged with 2,3-dioxabicyclo[2,2,1]heptene solution (22.7 mmole) kept at -78°C, and an addition funnel charged with glacial acetic acid (11.6 ml 0.2043 mole, 90% of the theoretical amount needed). After cooling the flask to -78°C, the acetic acid and peroxide were added simultaneously dropwise over a period of 20 min. The reaction mixture was green and no gas evolution was observed yet. The reaction mixture was stirred another 30
minutes at \(-78\) °C then the cold bath was removed and the reaction allowed to warm up to 0 °C. Gas evolution was observed at \(-10\) to 0 °C. The flask was placed in ice and the reaction stirred 2.75 hr. more. Very slow gas evolution occurred and the reaction mixture became lighter green. Solid KAD was still present. The reaction was stirred overnight under a slow nitrogen purge while surrounded with 1/4 in. copper coiled tubing immersed in water. The coils were cooled with a NESLAB cold bath set at \(+5\) °C. The KAD never completely disappeared.

Care was taken in working up the product to exclude water which reacts with the peroxide and to keep the peroxide cold. The reaction apparatus was disassembled keeping the reaction flask stoppered, purged with nitrogen, and in ice. The solids were filtered off using an aspirator and a 60 ml medium porosity fritted funnel. The filtrate was collected in an ice-cooled flask containing anhydrous sodium sulfate. The filter cake was kept solvent moist at all times. It was rinsed with three 10-15 ml portions of fresh, cold solvent and was destroyed by cautiously immersing it in a beaker of water (strong fizzing occurred). The light blue filtrate was poured into an ice-cooled 500 ml erlenmeyer flask containing anhydrous sodium sulfate. The solution was filtered quickly through fluted filter paper into a tared, taped, ice-cooled flask and the solvent removed by rotovap while cooling the flask in ice and the receiving flask with dry ice. Nmr showed that the blue-green liquid product was mainly peroxide (odor: rotten). Low temperature TLC at \(-20\) °C (dry ice-carbon tetrachloride) on silica gel with methylene chloride or 20% ethyl acetate-hexanes eluent and iodine, uv, and Fe(II) visualization showed peroxide and methylene blue to be the only two
components. Hence, low temperature column chromatography was not warranted. The product was bulb to bulb distilled (30 °C, 0.1 mm) collecting the yellow distillate at -78 °C. Low temperature recrystallization from 12-15 ml dry pentane at -78 °C four times yielded peroxide (0.1385g, 6% yield from cyclopentadiene, white crystals, mp 42-45.5 °C, lit mp 41-43 °C76, 42-43.5 82, 63-65 83). The NMR: (C₆D₆) δ 4.2 (2 H, s), 1.76-2.04 (1H, d of pentets), 0.80-1.76 (5H, m) matched the literature spectrum. 84 This unstable peroxide decomposed to yellow products with time even when stored in the freezer.

**Determination of the Densities of Peroxides**

A 100 microliter syringe containing about 50 μl peroxide was weighed on a five decimal place analytical balance (Dr. Margrave's lab). The peroxide was discharged from the syringe and the resulting peroxide-wet syringe weighed. The temperature of the lab was noted.

\[ d = \left[ \frac{(W_F - W_W)}{V} \right] \times 1000 \]
\[ d = \text{density in g/ml} \]

\[ W_F = \text{weight of the syringe (g) containing V μl of peroxide} \]

\[ W_W = \text{weight of the peroxide-wet but empty syringe} \]

The densities and molecular weights of the peroxides studied are shown in Table X. Literature densities 65 were used for ASC (1.013) and DTBP (0.794).

**General Procedure for Quenching Experiments Using Nitrogen Purged Solutions**

Sensitizer solution (3 ml) was syringed into a pyrex purge cell (1 X 1 cm i.d.) shown in Figure 16 fitted with two custom made teflon
stoppers and the solvent level in the cell was marked with a wax pencil. One stopper was solid and the other had a hole large enough to allow passage of a 20 gauge 16 cm long syringe needle. The lower 2.5 cm of the needle was bent slightly. The needle was connected via a small piece of tygon tubing, polyethylene tubing, and the luer lock connector from a broken 5 ml syringe to a tank of prepurified nitrogen as shown in Figure 17. The solution was purged while it was rotated in the holder shown in Figure 18 under the power of an inverted overhead stirring motor while the weight of the tubing was borne by a vertically mounted length of 3 cm glass tubing. At the end of the purge period, the needle was lifted and held above the solution for a few seconds while the solid stopper was placed into position and the holed stopper loosened. The holed stopper and syringe needle were removed as the solid stopper was placed on the cell.

Desirable purge rates gave reproducible lifetimes and minimum solvent losses. Two methods were used to decide whether the lifetimes were trustworthy. In both methods samples were purged for an optimum amount of time, $m$, which ranged from 5–20 min. METHOD ONE: A sample was purged for $m$ minutes and a lifetime was obtained. This process was repeated. If the two lifetimes were close, the data were trusted. METHOD TWO: Method one was done first, then the sample was deliberately opened to air and swirled, purged for $m$ minutes, and a lifetime obtained. If the lifetimes were close, the data were trusted.

Method one was used early in this work. It was repeated as many times as needed on sensitizer-only solutions, adjusting the purge rate, changing the purge time, and starting over when solvent losses were
Figure 16. Cell for the determination of triplet lifetimes by nitrogen purge.

Figure 17. Set up for nitrogen purging of solutions.

Figure 18. Holder for 1 cm cell used in nitrogen purging of solutions.
large until the optimum purge time was found. Then, quencher addition was begun and method one was applied only once after each addition of quencher. Method two was used towards the end of this work exclusively on sensitizer-only solutions. Once satisfactory sensitizer lifetimes were obtained, quencher addition was begun and the solutions were only purged once after each addition of quencher for the optimum minutes at the optimum purge rate.

Neat peroxide or a peroxide stock solution was added to the sensitizer solution sequentially with a microliter syringe. After purging, solvent losses and gains were measured in mm with a ruler from the mark placed on the cell at the beginning of the experiment. 1 mm = 0.1 ml solvent. Calculated quencher concentrations were corrected for solvent loss as needed. For an experiment with six different quencher concentrations, 0.3–0.5 ml was the maximum amount of solvent lost.

UV spectra were obtained for a given sensitizer solution without any quencher added and with the maximum amount of quencher added. The total absorbance at the laser excitation wavelength was measured. A total absorbance attributable as the expected value for the sum of the absorbance of the sensitizer and the peroxide was taken as evidence against any ground state chemistry between sensitizer and peroxide. Absorbance values attributable in this way occurred in all the peroxide-sensitizer systems we studied except as noted in Table II. Solvent loss effects were considered in calculating the total absorbance. Even though rather high peroxide concentrations were required in this work, (see data shown in the Stern-Volmer plots in Appendix A), peroxide absorbance at the excitation wavelength could be
kept low because of the low extinction coefficients of the peroxides. (See Table VIII.) This minimized direct irradiation of the peroxides.

**Preparation of Samples for Laser Flash Photolysis**

Sensitizer and peroxide solutions were prepared using an analytical balance, volumetric flasks, and pipettes. Glassware was rinsed at least four times with reagent methanol, soaked in an Alconox soap solution, rinsed ten times with water (the last rinse was with deionized water) and dried in an oven.

Samples were either degassed in the 1 cm pyrex cells shown in Figure 19 or purged according to the general purging procedure. Good quenchers such as 221 were present in low enough concentrations to be appreciably destroyed by energy transferred from sensitizer after 10 laser pulses. In that case, individual cells of different peroxide concentrations were degassed and first flash data were obtained. Sensitizer solutions were prepared with an absorbance of one at the laser wavelength.

![Diagram](image)

**Figure 19. Degassing cell**

**Laser Flash Photolysis**

Sensitizer solutions were excited with a Lambda Physik EMG 101 excimer laser. Ten laser pulses gave satisfactory decay curve data and
were normally used. The output wavelength depended on the gas mixture charged in the laser. 337 nm (nitrogen) and 351 nm (xenon/fluorine) were used in this work. Gases came from Big 3 Industries, Inc. (P. P. nitrogen), Air Products (helium), and Cryogenic Rare Gas Laboratories, Inc. (5% fluorine in helium, 99.99% xenon). Typical pulse energies were \(1.3 \times 10^{-6}\) me/pulse (337 nm) and \(4.5 \times 10^{-5}\) me/pulse (351 nm). Because determination of a typical lifetime required only 10 laser pulses, cooling water was not needed.

The monitoring lamps were an Osram XBO 150 W/S 150 watt xenon lamp housed in a Photochemical Research Associates, Inc. (PRA) water cooled ALH215 Arc Lamp Housing powered by a PRA M303 Lamp Supply or a Sears MY5716 quartz-halogen lamp housed in a homemade lamp housing powered with a home-built 12V power supply. The xenon lamp intensity at different wavelengths is shown in Figure 20 and that of the quartz-halogen tungsten lamp is shown in Figure 21.

After passing through the sample cell, the analyzing light traveled through a lens and a Bausch and Lomb Cat. No. 33-86-07 1200 grooves/mm grating monochromator. Transmitted intensity was monitored by a 1P28 photomultiplier tube powered by a EMI Gencom, Inc. programmable Series HM-1500N power supply normally set at 900V. The PMT socket was wired for nanosecond response using the circuit of Porter and West except that our system used a 2.2 k output resister instead of 50 ohms. The result is a slightly slower response time but a larger PMT signal voltage in our system. The PMT output was driven into the 50 ohm input of a LeCroy 2256AS 20MHz Waveform Digitizer by an Analog Devices 50J op amp. A short length (11 in.) of RG-59 cable which had a time
constant of 2.2 RC (R = 1 k, C = 17 pf/ft, op amp input time constant = 37 nsec) connected the op amp and the PMT.

The digitizer was housed in a Standard Engineering Corporation (SEC) Ultima 3000 crate controlled by a SEC MIK-11/2C camac system Microprocessor. Additional components of the computer system were a MIK-11 Data Bus, a MIK-11 Memory 300220, a Peripheral Adapter Interface to a Data Systems Design, Inc. DSD-440 dual double density, single side Flexible Disk System, and a FLV11-J Quad Asynchronous Serial Port which allowed communication between the microcomputer and the departmental PDP 11/70. An RT-11 operating system was used. Data were stored on 8 in. Data Systems critically tested floppy disks. [NOTE: A large number of bad blocks occurred when cheaper disks were used]. Experiments were conducted interactively with a Hewlett Packard HP2648A graphics terminal which also displayed the data.

A Bi Ra Systems Inc. Model 5301 ADC analog to digital converter was used to read the steady state PMT output, the op amp output during nulling, and the pulse energy from an Evans Associates Model 4130 gated integrator. A Joerger Model D/A-12 digital to analog converter was used to send nulling voltages to the op amp. A Joerger Model OR-3 Output Register provided the necessary digital switching.

A Hewlett Packard 1741A 100MHz oscilloscope displayed the PMT output and a critical timing pulse. Two volt PMT outputs were desirable for a good S/N ratio so the analyzing light was chopped with a homemade chopper to prevent burning out the PMT.

Pulse energies were monitored with a Silicon Detector Corporation SD100 uv photodiode. Relative pulse energies were monitored during an
experiment and during the lifetime of a laser charge but the numbers were never actually calibrated. Pulse energies were found to be constant within 1% during a typical experiment lasting several hours.

Other equipment included a 3 cm path length quartz cell filled with water placed between the xenon lamp and the sample to filter out infrared irradiation, a cylindrical lens or up to three fine mesh brass screens placed between the laser and the sample to adjust the beam intensity incident on the sample, a home-built mechanical shutter placed between the xenon lamp and the sample, and a Lambda Physik vacuum pump for handling the laser gases.

A top view of the laser flash photolysis set-up is shown in Figure 22a while the computer system is shown in Figure 22b. The circuits are in Appendix C. The FORTRAN program LASFPH, FOR obtained laser flash photolysis data (see Appendix D). Spectra were obtained using the program KOMSPC,FOR (see Appendix D) and a Superior Electric MO62-FC03 stepper motor. A special version of KOMSPC,FOR was used when storage of individual decay curves used to obtain a spectrum was desired (see Appendix D). Old spectra were viewed on the graphics terminal with the program SEPPLT,FOR (see Appendix D).

Mixed first and second order data analysis was obtained with the program LSMIX,FTN on the departmental PDP 11/70 computer (see Appendix D). The unformatted data files created by LASFPH, FOR were formatted with the program LSWRFM,FOR (see Appendix D) then transferred to the 11/70 using the EXF and [11,2]FXFER file handling programs. LSMIX,FTN generates a huge file suitable for generating plots of the data with the PDP 11/70 programs, [11,2]AUTHPP and [11,2]HPF (see LSMIX,FTN program
Key to Figure 22a

10 = PMT power supply
11 = monochromator
12 = stepping motor
13 = PMT
14 = op amp box
15 = xenon lamp
16 = op amp power supply and manual override control box
17 = mechanical shutter
18 = filter (H$_2$O)
19 = chopper
20 = chopper motor
21 = chopper alignment sensor
22 = pipe

23 = lens
24 = cell holder
25 = sample cell
26 = screens or spherical lens
27 = platform
28 = pulse energy monitor
29 = laser output
30 = stepper power supply
31 = xenon lamp power supply
32 = pulse energy monitor and timing logic box
33 = oscilloscope
34 = cooling water filter
Figure 22b. Diagram of the laser flash photolysis computer system.

1 = D/A-12
2 = BiRa ADC
3 = OR-3 output register
4 = LeCroy digitizer
5 = Data Bus
6 = MIK-11/2C microprocessor
7 = Memory for MIK-11/2C
8 = Floppy disk drive interface
9 = PLV11-J Quad Asynchronous Port
listing for plots available).

Hints
1. Make sure the Le Croy and floppy disk drive are off when starting the xenon lamp; otherwise the disk drive or microprocessor hang due to lamp electrical interference.
2. Use a solution of a compound that fluoresces in the visible region to check for laser-sample cell alignment e.g. 9-fluorenone.
3. The timing patterns on the scope should look like this:

```
+------+
|     |
|     |
|     |
+------+

PMT

Timing
```
Odd patterns indicate that the chopper alignment phototransistor is misaligned or that analyzing light is hitting this sensor.
4. Nitrogen charges can be used for a week. Some falloff in laser pulse energy occurs each day. Xenon-fluorine charges can only be used for a few days and even then pulse energy falls rapidly.
5. The correct oscilloscope settings are recorded in Notebook IV p. 31.

The accuracy of our system was checked by flashing benzene solutions of 2-acetonaphthone and trans-stilbene. Our \( k_q (3.13 \times 10^9 \text{ M}^{-1} \text{sec}^{-1}) \) agreed reasonably well with Hammond and Herkstroeter's value.
The Stern-Volmer plot is shown in Appendix A. Purged solutions were found to give satisfactory results for triplets. A $k_q$ for ascaridole and 2-acetonaphthone in degassed cells ($4.76 \times 10^7$ M$^{-1}$ sec$^{-1}$) agreed with the value obtained in a nitrogen purged cell ($4.78 \times 10^7$ M$^{-1}$ sec$^{-1}$).

**Biacetyl Quenching Studies**

Biacetyl triplet phosphorescence lifetimes were measured by means of an air spark lamp (pulse duration = 5 μsec), a monochromator (520 nm) perpendicular to the lamp, and a PMT (1P28, wired for μsec response). A CuSO$_4$/NH$_4$OH filter was placed between the sample and the lamp. The PMT output was sent to a six bit Biomation Transient Digitizer Model 610B which was interfaced by a home-built interface to the PDP 11/70. The computer program BIO,FTN by Dr. J. V. V. Kasper acquired the phosphorescence emission data and it was worked up by first order data analysis with the computer program LAT,FTN. Benzene solutions of biacetyl (0.009 M) were placed in 1 x 1 cm cells shown in Figure 23. The ChemVac glass-piston-teflon-sealed stopcock allowed sequential quencher addition to one cell. A sample was degassed and a lifetime obtained. Then the sample was frozen in liquid nitrogen while nitrogen gas was introduced via the apparatus shown in Figure 24. The cell was opened and neat peroxide or peroxide stock solution was added with a microliter syringe. The sample was degassed and a new lifetime was obtained. This process was repeated until phosphorescence decay data were obtained for several different peroxide concentrations. Values of $k_q$ were obtained from the Stern-Volmer equation as for laser flash photolysis. A linear Stern-Volmer plot (see Appendix A) for biacetyl and DTBP was finally
Figure 23. Chem Vac cell for sequential quencher addition.
1 Matheson pressure gauge  
Part No. P/N 63-3104  
30 in. vacuum to 30 psig

2 metal to glass connection  
Thomas A. Read  
Part No. G321-4-GX-2

brass pipe and swagelok fittings used

Figure 24. Apparatus for introduction of nitrogen into Chem Vac cells.
obtained by this method after previous attempts with separate degassed tubes gave scattered plots.
DIFFERENTIAL SCANNING CALORIMETRY (DSC) TRACE

SCREEN
4-MAR-82  5:12
SCREEN
DYN/ISO  1/2     1
START     25
END
BASELINE TYPE  1
PLOT CM  15
PLOT MODE  1

END TEMP.  °C  247.0

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL-->

50.000  mW

2-phenylethyl peroxide
DSC DATA ANALYSIS

KINETIC ANALYSIS

KINETIC ANALYSIS
AUTOLIMIT 0/1
START TEMP. °C 100
END TEMP. °C 100
BASELINE TYPE 3
ALPHA START 0.1
ALPHA END 0.8
PLOT CM 10
PLOT MODE SINGLE ALPHA
APPLIED KINETICS ISO/AD 1/2
PLOT CM 10
AT TABLE K 10
START TEMP. °C 100
END TEMP. °C 100
ALPHA END 0.5

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL

8.18 M J

AH EXG J/G 18477
SH J/G 724.92
SINGLE T. °C 150.3
REACT. ORDER .76
CONF. LIMIT .03

E O KJ/MOL 143.67
CONF. LIMIT 34.39
LN K
CONF. LIMIT 1.17

T °C LN K P W/KG T MIN.
100.0 - 5.72 3743.1
101.0 - 16.92 39.0 1123.3
102.0 - 11.25 174.7 753.5
103.0 - 9.31 174.7 129.8
104.0 - 7.25 183.6 42.8
105.0 - 6.29 139.0 16.8
106.0 - 5.35 344.2 4.2734
107.0 - 4.46 234.6 2.5364
108.0 - 3.61 192.72 1.9955
109.0 - 2.76 448.9 1.7776
110.0 - 1.99 701.4 1.2178

2-phenylethyl peroxide
DIFFERENTIAL SCANNING CALORIMETRY (DSC) TRACE

SCREEN
3-JUL-82  60:06
SCREEN 1/2
DYN/ISO 120
START 240
END 1
BASELINE TYPE CM 10
PLOT MODE 1

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL -->

10,000 W

dihydroascaridole
DSC DATA ANALYSIS

KINETIC ANALYSIS

3-JUL-82 40144

KINETIC ANALYSIS
ANALYZE 8/1
START TEMP. °C 150
END TEMP. °C 240
BASELINE TYPE 8
ALPHA START 0.1
ALPHA END 0.8
PLOT CM 10
PLOT MODE 101
SINGLE ALPHA 0.1
APPLIED KINETICS 10/2
PLOT CM 0
AT TABLE X 10
START TEMP. °C 120
END TEMP. °C 250
ALPHA END 0.7
END TEMP. °C 254.7

TEMPERATURE °C

HEAT FLOW
EXOTHERMAL--)

10.000 W

M J
 Hod

SINGLE T. °C 196.3
REACT. ORDER
CONF. LIMIT .49
E A .149.11
CONF. LIMIT 1.48
LNM LIMIT 31.92

T °C LN K P W/kg * MIN.

120.0 - 14.56 59374
120.0 - 13.43 18019
140.0 - 12.33 4495.8
160.0 - 11.33 2295.4
180.0 - 10.33 846.57
190.0 - 9.41 103.9 338.81
190.0 - 8.50 251.7 198.94
190.0 - 7.66 592.9 59.919
200.0 - 6.84 1242.7 23.976
210.0 - 6.06 3943.3 11.888
220.0 - 5.34 4631.1 3.3098
230.0 - 4.63 18884 2.7471
240.0 - 3.99 33258 1.3539
250.0 - 3.32 58379 .49644
260.0 - 3.58 95847 .36391

Dihydroascaridole
APPENDIX A

STERNE–VOLMER PLOTS
**Graph 1:**

ASCARIDOLE  
P-METHOXYACETOPHENONE  
SOLVENT: BENZENE

1/TAU sec⁻¹ /10²

[PEROXIDE] M /10⁻²

**Graph 2:**

ASCARIDOLE  
TRIPHENYLENE  
SOLVENT: BENZENE

1/TAU sec⁻¹ /10²

[PEROXIDE] M⁻¹ /10⁻²
2.2.1 PEROXIDE

**p-METHOXYACETOPHENONE**

**SOLVENT: Benezene**

\[
\frac{1}{\tau} \text{ sec}^{-1} / 10^1
\]

**[PEROXIDE] M / 10^{-3}**

---

2.2.1 PEROXIDE

**TRIPHENYLENE**

**SOLVENT: Benezene**

\[
\frac{1}{\tau} \text{ sec}^{-1} / 10^1
\]

**[PEROXIDE] M / 10^{-3}**
2.2.1 Peroxide

- Thioxanthone
- Solvent: Benzene

\[ \frac{1}{\tau} \text{ sec}^{-1} / 10^2 \]

\[ \frac{1}{\tau} \text{ sec}^{-1} / 10^2 \]

\[ \frac{[\text{peroxide}]}{M / 10^{-3}} \]

\[ \frac{[\text{peroxide}]}{M / 10^{-2}} \]
1/TAU sec$^{-1}$/10$^1$

DI-tert-BUTYL PEROXIDE
2-ACETONAPHTHONE
SOLVENT: BENZENE

[PEROXIDE] M

1/TAU sec$^{-1}$

BIACETYL
DI-tert-BUTYL PEROXIDE
SOLVENT: BENZENE

[PEROXIDE] M /10$^{-1}$
1/TAU sec⁻¹ / 10²

[PEROXIDE] M / 10⁻¹

tert-BUTYLPERBENZOATE
p-METHOXYACETOPHENONE
SOLVENT: BENZENE

1/TAU sec⁻¹ / 10²

[PEROXIDE] M

tert-BUTYLPERBENZOATE
2-ACETONAPHTHONE
SOLVENT: BENZENE
APPENDIX B

MISCELLANEOUS PHOTOCHEMICAL EXPERIMENTS

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The purpose of the first two experiments described in this appendix was to observe independently reactive intermediates possibly present in Elad's system and to determine the quenching rate constants for these intermediates by peroxides, especially, DTBP.

1. $k_q$ Values for Peroxides and Ketyl Radicals

Flash photolysis was done with an older kinetic spectroscopy apparatus (pulse duration = 15 µsec) on degassed solutions of biacetyl (0.012M) in isopropanol. Two changes were made in the way flash photolysis was done. Instead of using a strip chart recorder, data were acquired with the Biometion Transient Digitizer Model 610B and the computer program BIO.FTN as in the biacetyl work. The 17 cm pathlength flash photolysis cells were equipped with Chem Vac stopcocks and quencher was added sequentially using the nitrogen introduction apparatus shown in Figure 24 and the procedure described for biacetyl in the experimental. A long-lived intermediate was observed ($\tau \sim 2$ msec) at the reported wavelength (330 nm) for biacetyl ketyl radical. The experiment was repeated with degassed isopropanol solutions of biacetyl and peroxides. Mixed first and second order data analysis led to $k_q$ values for DTBP ($2.4 \times 10^6$, $8.4 \times 10^5$ M$^{-1}$ sec$^{-1}$ on separate runs) and ASC ($4.6 \times 10^6$ M$^{-1}$ sec$^{-1}$). The results mean that in Elad's system, biacetyl triplet ($k_q = 1.4 \times 10^5$ M$^{-1}$ sec$^{-1}$) and biacetyl ketyl radical are quenched at comparable rates and since the ketyl radical lives longer than biacetyl triplet, a chemical sensitization mechanism cannot be ruled out. See Calculation I at the end of this appendix.

Attempts were made to observe biacetyl ketyl radical in isopropanol with the laser flash photolysis system. However, both 337
and 351 are inconvenient exciting wavelengths. In order for biacetyl to have an absorbance of one at these wavelengths, the ground state absorbance at the most favorable analyzing wavelength (330 nm) is so high that almost no analyzing light passes through the sample. No ketyl radical was seen for that reason. The older kinetic spectroscopy apparatus used xenon lamps which excited biacetyl over its entire absorption spectrum; hence, more dilute solutions could be used.

Attempts to observe the long-lived ketyl radical in benzene solutions containing Elad's typical toluene concentration (1.42 M) with the older flash kinetic spectroscopy apparatus failed. A transient was seen, but its short lifetime (98 μsec) suggested that the transient was biacetyl triplet which is known to absorb in the same region. We decided to investigate whether peroxide quenching of ketyl radicals was a general process. Benzil ketyl radical was generated by flashing degassed isopropanol solutions of benzil (6.8 x 10^-3 M) with the older apparatus (λ_analyze = 490 nm, τ = 4-10 msec). A relatively large amount of DTBP (0.1 M) was added to the solution but no quenching was observed.

2. Benzyl Radical

We were able to observe a long-lived transient (τ_1/2 = 700 μsec, second order decay, k_2 = 3.4 x 10^8 M^-1 sec^-1, assuming ε_318 = 1100 M^-1 cm^-1, λ_analyze = 453, 318 nm) upon flashing benzene solutions of dibenzyl ketone (8.7 x 10^-4 M) with the older flash apparatus. Strong quenching was observed with 0.1 M DTBP. Turro has recently used this method to generate benzyl radical by laser flash photolysis.
3. DTBP Quantum Yield Studies

Degassed solutions of DTBP plus biacetyl or benzophenone in either benzene or toluene in cylindrical pyrex cells were irradiated at 366 nm in a merry-go-round apparatus. The disappearance of DTBP and biacetyl and the appearance of acetone and tert-butanol were determined by GC with a Barber-Coleman instrument (250 ft. metal capillary SF-96 column at 25 °C, FID detection). α,α,α-Trifluorotoluene was the internal standard and was present in the samples during irradiation. Sharp peaks were obtained and peak heights were used in the data analysis. Peak heights were within 1-7% of the average peak height for the three injections made for each sample. Light intensity was determined by azo-tert-butane actinometry. Both biacetyl and benzophenone sensitized DTBP decomposition, but the quantum yields were low (0.04-0.10) in two separate experiments. The quantum yield for DTBP decomposition with biacetyl in benzene was a factor of ten lower than Elad's\textsuperscript{16} value. Our low quantum yields were surprising since DTBP is known to break apart to two tert-butoxy radicals upon direct irradiation with almost unit efficiency.\textsuperscript{18} Also, using diphenylmethanol as a probe, Scaiano and Wubbels\textsuperscript{30} determined that 70% of the quenching events that occur between DTBP and the triplet states of p-methoxypropiophenone, benzophenone, or naphthalene led to the production of two tert-butoxy radicals. Our low quantum yields for sensitized DTBP decomposition are not in agreement with such an efficient process. A sensitizer-DTBP exciplex could form prior to energy transfer from sensitizer to DTBP in our system. Decay of this exciplex to ground state sensitizer and DTBP would lower the efficiency of DTBP decomposition to radicals. We have
no experimental evidence to support the intermediacy of such an exciplex in our system. Furthermore, it would be strange if our system requires an exciplex while Elad's more complex system which includes a peptide does not. The experimental conditions and quantum yields for the two experiments are shown in Tables XI-XIV.

4. 9,10-Dicyanoanthracene and Peroxides

Ascaridole possesses such a low ionization potential \(^8^9\) (8.42 eV) compared with other peroxides (8.79 eV for DTBP) that the possibility of electron transfer from ascaridole to a good electron-accepting singlet sensitizer was investigated. Fluorescence spectra (\(\lambda_{\text{excite}} = 423\) nm; \(\lambda_{\text{emit}} = 435, 458\) nm) in acetonitrile of degassed solutions of 9,10-dicyanoanthracene (DCA), (4.9 \(\times\) \(10^{-6}\) M) were obtained in a 1 cm pyrex cell like the one shown in Figure 23 to allow nitrogen introduction with the apparatus shown in Figure 24 and sequential peroxide addition. Values of \(k_q\) were obtained for ascaridole (2.52 \(\times\) \(10^9\) M\(^{-1}\) sec\(^{-1}\)) and DTBP (5.87 \(\times\) \(10^6\) M\(^{-1}\) sec\(^{-1}\)) from Stern-Volmer plots and the literature singlet lifetime \(^9^0\) (15.3 nsec) of DCA. The plot for ascaridole is shown in Figure 25. Corrections were made for the small concentration changes after quencher addition and for trivial absorbance of the peroxide at the excitation wavelength. The almost diffusion-controlled rate constant for ASC encouraged us to try this peroxide as a quencher of singlet anthracene, which should have a lower tendency to gain an electron. The anthracene \(k_q\) (1.34 \(\times\) \(10^9\) M\(^{-1}\) sec\(^{-1}\)) was also large. We saw no way, at the time, to decide between diffusion-controlled singlet energy transfer and electron transfer in these compounds so abandoned this line of pursuit.
Figure 25. Stern-Volmer plot for 9,10-dicyanoanthracene + ascaridole.
Table XI

Experiment I DTBP Photolysis Conditions

<table>
<thead>
<tr>
<th>Tube</th>
<th>Solvent</th>
<th>Sensitizer</th>
<th>[sensitizer]</th>
<th>[DTBP]</th>
<th>[ΦCF$_3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ΦH</td>
<td>Φ$_2$CO</td>
<td>0.007</td>
<td>0.199</td>
<td>0.0383</td>
</tr>
<tr>
<td>2</td>
<td>ΦCH$_3$</td>
<td>Φ$_2$CO</td>
<td>0.007</td>
<td>0.198</td>
<td>0.0397</td>
</tr>
<tr>
<td>3</td>
<td>ΦH</td>
<td>biacetyl</td>
<td>0.170</td>
<td>0.199</td>
<td>0.0383</td>
</tr>
<tr>
<td>4</td>
<td>ΦCH$_3$</td>
<td>biacetyl</td>
<td>0.175</td>
<td>0.204</td>
<td>0.0397</td>
</tr>
</tbody>
</table>

a Sensitizer absorbance was 0.25 at 366 nm.
90 minute irradiation time.
Cells made of 7 mm o.d. tubing. Pathlength was 5 mm.
Conversion was 4-9%.

Table XII

Experiment I Quantum Yield Results

<table>
<thead>
<tr>
<th>Tube</th>
<th>Φ - biacetyl</th>
<th>Φ - DTBP</th>
<th>Φ - acetone</th>
<th>Φ - tert-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0.096</td>
<td>0.064$_b$</td>
<td>0.12$_b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14$_b$</td>
<td>0.093$_b$</td>
<td>0.17$_b$</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
<td>0.072</td>
</tr>
<tr>
<td>3$^c$</td>
<td>0.082</td>
<td>0.055$_b$</td>
<td>0.073$_b$</td>
<td>0.072$_b$</td>
</tr>
<tr>
<td></td>
<td>0.11$_b$</td>
<td>0.072$_b$</td>
<td>0.096$_b$</td>
<td>0.094$^b$</td>
</tr>
<tr>
<td>4$^c$</td>
<td>0</td>
<td>0.084</td>
<td>-</td>
<td>0.19</td>
</tr>
</tbody>
</table>

a All Φ's are corrected for the actual fraction of light absorbed.
b Φ's are corrected for the calculated efficiency of energy transfer from sensitizer to peroxide.
c The value of Φ - acetone + Φ - tert-butanol is greater than two times the value of Φ - DTBP for this tube. This is an unexpected and suspicious result.
Table XIII

Experiment II DTBP Photolysis Conditions\(^{a}\)

<table>
<thead>
<tr>
<th>Tube</th>
<th>Solvent</th>
<th>Sensitizer</th>
<th>[sensitizer]</th>
<th>[DTBP]</th>
<th>[(\Phi_{CF_3})]</th>
<th>(\Phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(\phi H)</td>
<td>(\phi_2 CO)</td>
<td>0.014</td>
<td>0.2</td>
<td>0.16</td>
<td>(\Phi)</td>
</tr>
<tr>
<td>2</td>
<td>(\phi H)</td>
<td>bisacetyl</td>
<td>0.340</td>
<td>0.2</td>
<td>0.16</td>
<td>(\Phi)</td>
</tr>
<tr>
<td>3</td>
<td>(\phi CH_3)</td>
<td>(\phi_2 CO)</td>
<td>0.014</td>
<td>0.2</td>
<td>0.16</td>
<td>(\Phi)</td>
</tr>
<tr>
<td>4</td>
<td>(\phi CH_3)</td>
<td>bisacetyl</td>
<td>0.340</td>
<td>0.2</td>
<td>0.16</td>
<td>(\Phi)</td>
</tr>
</tbody>
</table>

\(^{a}\) Sensitizer absorbance was 1.0 at 366 nm. 130 minute irradiation time. Cell pathlength was 1 cm. Conversion was 4-10% with the exception of Tube 3 which gave an unusually low 0.4%.

Table XIV

Experiment II Quantum Yield Results

<table>
<thead>
<tr>
<th>Tube</th>
<th>(\Phi)-bisacetyl</th>
<th>(\Phi)-DTBP</th>
<th>(\Phi)-acetone</th>
<th>(\Phi)-tert-butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0.084</td>
<td>0.070</td>
<td>0.078</td>
</tr>
<tr>
<td>2(^{a})</td>
<td>0.019</td>
<td>0.040</td>
<td>0.071</td>
<td>0.051</td>
</tr>
<tr>
<td>3(^{a})</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
<td>0.067</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.087</td>
<td>-</td>
<td>0.15</td>
</tr>
</tbody>
</table>

\(^{a}\) The value of \(\Phi\)-acetone + \(\Phi\)-tert-butanol is greater than two times the value of \(\Phi\)-DTBP for this tube. This is an unexpected and suspicious result.
Calculation I: Extent of ketyl radical involvement in Elad's biacetyl-DTBP-tert-butanol system.

Three assumptions are necessary: 1.) Our \( k_q \) for biacetyl ketyl radical and DTBP determined in isopropanol is the same in Elad's solvent, tert-butanol; 2.) The lifetime of biacetyl triplet in isopropanol is 20 \( \mu \text{sec} \) as estimated from the work of Singh et. al.\(^{19}\); 3.) The value of the rate constant for abstraction of a hydrogen atom from toluene by biacetyl triplet is \( 1 \times 10^4 \text{ M}^{-1} \text{ sec}^{-1} \)^{20}

\[
\tau_0 = 20 \mu \text{sec} \quad k_{\text{deact}} = 5 \times 10^4 \text{ sec}^{-1}
\]

\[
\text{biacetyl}^* + \text{DTBP} \quad k_q = 1.4 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}
\]

\[
k_r = 1 \times 10^4 \\
0.274 \text{ M isopropanol}
\]

\[
\text{biacetyl ketyl radical} \quad 1.42 \text{ M } \varphi \text{CH}_3
\]

\[
\tau_0 = 2 \text{msec} \quad k_{\text{deact}}' = 5 \times 10^2 \text{ sec}^{-1}
\]

\[
\text{isopropanol}
\]

\[
\text{deactivation}
\]

\[
\text{DENOM} = 5 \times 10^4 + 0.274(1.4 \times 10^5) + 1.42(1 \times 10^4) = 1.026 \times 10^5
\]

\[
3.84 \times 10^4
\]

\( F_1 \) = fraction of biacetyl\(^*\) that decays by energy transfer to DTBP.

\( F_2 \) = fraction of biacetyl\(^*\) that undergoes deactivation.

\( F_3 \) = fraction of biacetyl\(^*\) that becomes biacetyl ketyl radical.
\[ F_1 = \frac{3.84 \times 10^4}{\text{DENOM}} = 0.37 \]
\[ F_2 = \frac{5 \times 10^4}{\text{DENOM}} = 0.49 \]
\[ F_3 = \frac{1.42 \times 10^4}{\text{DENOM}} = 0.14 \]
\[ \text{TOTAL} = 1.00 \]

\[ F_4 = \text{fraction of ketyl radical that interacts with DTBP} \]
\[ F_4 = \frac{0.274 \times 1.6 \times 10^6}{0.274(1.6 \times 10^6) + 5 \times 10^2} = 0.99 \]

All three fates of biacetyl triplet (deactivation, energy transfer to DTBP, and ketyl radical formation) occur in significant amounts. Triplet energy transfer to DTBP occurs roughly 2.5 times as often as ketyl radical formation (37% vs. 14% of the time) but ketyl radical formation is important. Furthermore, once ketyl radical forms, it is quenched by DTBP with almost unit efficiency. Hence, ketyl radical involvement cannot be ruled out in Elad's system. DTBP-ketyl radical interaction by a presumed chemical sensitization mechanism could contribute significantly to the total DTBP decomposition to tert-butoxy radicals. Biacetyl triplet energy transfer to DTBP is the other contributor to DTBP decomposition. In Elad's system, the latter makes the larger contribution.
**Calculation II:** Extent of ketyl radical involvement in Smith's benzophenone-benzoyl peroxide-benzene system.

\[ \tau_0 = 10 \ \mu\text{sec} \quad k_{\text{deact}} = 1 \times 10^5 \ \text{sec}^{-1} \]

\[ \text{benzophenone}^* + \text{BP} \quad k = 1.4 \times 10^6 \]

\[ \text{Smith} \quad 0.07 \ M \quad \text{Smith} \]

\[ k_z = 16.4 \ M^{-1} \ \text{sec}^{-1} \quad \phi \text{H} \]

\[ \text{Schuster} \quad \text{solvent} = 11.2 \ M \]

\[ \text{benzophenone ketyl radical} \]

\[ \text{DENOM} = 1 \times 10^5 + 0.07(1.4 \times 10^6) + 11.2(16.4) = 1.98 \times 10^5 \]

\[ 9.8 \times 10^4 \quad 183 \]

\[ F_1 = \text{fraction of benzophenone}^* \quad \text{that becomes ketyl radical.} \]

\[ F_2 = \text{fraction of benzophenone}^* \quad \text{that transfers energy to BP.} \]

\[ F_3 = \text{fraction of benzophenone}^* \quad \text{that deactivates.} \]

\[ F_1 = \frac{183}{\text{DENOM}} = 0.00092 \]

\[ F_2 = \frac{9.8 \times 10^4}{\text{DENOM}} = 0.49 \]

\[ F_3 = \frac{1 \times 10^5}{\text{DENOM}} = 0.50 \]

\[ \text{TOTAL} = 0.99 \]
APPENDIX C

LASER FLASH PHOTOLYSIS APPARATUS

List of Circuits

Logic to synchronize laser flash photolysis experiment
to analyzing light chopper .................................. 113
Stepper motor controller and tungsten lamp power
supply .......................................................... 114
Op amp box .................................................... 115
Op amp power supply and manual override (control box) 116
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CAMAC crate component specifics

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Explanation of DAC and ADC input and conversion
to volts ..................................................... 123

NOTE: Two abbreviations were used in the circuit diagrams

for microfarad. They are mF and mf.
Logic to Synchronize Laser Flash Photolysis Experiment to Analyzing Light Chopper
Stepper Motor Controller and Tungsten Lamp Power Supply
Photomultiplier Tube Socket
EMI HM1500N Power Supply

Photomultiplier Power Supply
Fire Laser and Read Pulse Energy Timing Diagram

Note: The letters E-N designate pulses shown on the Logic to Synchronize ...Chopper circuit diagram.
Timing Diagram to Read Op Amp and Photomultiplier Outputs
## Pinout of OR-3 output register Cannon DB52P

<table>
<thead>
<tr>
<th>channel</th>
<th>collector</th>
<th>emitter</th>
<th>bias</th>
<th>use</th>
<th>configuration&lt;sup&gt;a&lt;/sup&gt;</th>
<th>voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>18</td>
<td>36</td>
<td>fire laser</td>
<td>ge</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>19</td>
<td>37</td>
<td>open shutter</td>
<td>ef</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>20</td>
<td>38</td>
<td>unused</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>21</td>
<td>39</td>
<td>reset gated integrator</td>
<td>ge</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>22</td>
<td>40</td>
<td>op amp output relay stepper power</td>
<td>ge</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>23</td>
<td>41</td>
<td>enable BiRa start convert stepper-clockwise</td>
<td>ge</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>24</td>
<td>42</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>25</td>
<td>43</td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>26</td>
<td>44</td>
<td>stepper-counter clockwise</td>
<td>ge</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup> ge = grounded emitter; ef = emitter follower
Explanation of DAC and ADC Input and Conversion to Volts

The Joerger Digital to Analog Converter (Model DA-12) is set for offset binary input and an output range of -5 to +5 volts.

<table>
<thead>
<tr>
<th>Value which computer writes to DAC</th>
<th>Resulting output voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+5V</td>
</tr>
<tr>
<td>2048</td>
<td>0</td>
</tr>
<tr>
<td>4096</td>
<td>-5</td>
</tr>
</tbody>
</table>

The Bi Ra analog to digital converter (Model 5301) is set for a voltage input range of -5.12 to +5.12 volts and its output is in two's complement.

<table>
<thead>
<tr>
<th>Input voltage to Bi Ra</th>
<th>Value written to computer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>+5.00</td>
<td>2000</td>
</tr>
<tr>
<td>+5.12</td>
<td>2048</td>
</tr>
<tr>
<td>-5.12</td>
<td>4095</td>
</tr>
</tbody>
</table>

This is the input conversion formula to make DAC output equal to minus the Bi Ra input over the input range 0 to +5 volts.

\[ V_{DAC} = (V_{ADC} + 1995) \times 1.024 \]

where:
- \( V_{DAC} \) = Value which must be written to DAC
- \( V_{ADC} \) = Value written by Bi Ra to computer

The constant, 1995, gave more accurate output voltages than the mathematically derived constant, 2000.
APPENDIX D

COMPUTER PROGRAMS

Laser Flash Photolysis

LASFPH.FOR main program

Subroutines

APAGE,FOR
AVBGSB.FOR
AVGETC,FOR
AVGPLT,FOR
AVGSET,FOR
AVLTSQ,FOR
AVSETX,FOR
AVSNAP,FOR
COOL,FOR
FLCLCR,FOR
FLPLT,FOR
FLSCL,FOR
FLSCTY,FOR
JERITD,MAC
LACTU,FOR
PAGE,FOR
TDABOR,FOR
TDFPCO,FOR
TDGCR,FOR
TDGFNA,FOR
TTONOF,MAC
WAITF,MAC

In addition CBLOCK,MAC, CSGA,MAC, CSSA,MAC, and CDREG,MAC are used from the CAMAC object library, CMCLIB.OBJ. They are not listed here.

LASLIB.COM is a command file that creates the library of subroutine object files needed for LINK of LASFPH

LASFPH.TXT is a text file that explains the LINK of LASFPH

Transient Absorption Spectra

KOMSPC.FOR main program

Subroutines

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ITD_MAC ........................................... 152
PAGE.FOR .......................................... —
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SPECTRA.TXT explains the LINK of KOMSPC .......... 166

SEPPLT.FOR plots the old spectra generated by KOMSPC.FOR
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exception.

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CHKSPC.FOR allows the user to view the individual decay
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and Sarkanen

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LSRFM,FOR reads in LASFPH,FOR generated unformatted data files
and writes out formatted files suitable for FXFER file
transfer. . . . . . . . . . . . . . . . . . . . . . . . 190
PROGRAM LASFPH

THIS PROGRAM DOES PURE FIRST OR PURE SECOND ORDER FITTING FOR FLASH
PHOTOLYSIS DATA. IT ALSO AVERAGES DATA IN GROUPS OF THREE CHANNELS.
DATA VER/3.15/

PROGRAM VERSION SEPT. 8. 1981

LASFPH - TRANSIENT DIGITIZER HANDLER PROGRAM FOR LASER FLASH PHOTOLYSIS

AUTHORS: GREG LIVERMAN, TREACY WOODS, P. S. ENGEL

A GENERAL PURPOSE HANDLER PROGRAM FOR THE LECROY 2256AS TRANSIENT
DIGITIZER. AN INTERACTIVE PROGRAM DESIGNED TO RETRIEVE STORED
WAVEFORMS FROM THE 2256AS AND DISPLAYING THEM ON THE HP 2648A
GRAPHICS TERMINAL. THE WAVEFORMS CAN ALSO BE STORED IN A FILE
FOR LATER REFERENCE.

THE PROGRAM STARTS A CONVERSION CYCLE ON THE TRANSIENT DIGITIZER
AND WAITS FOR AN EXTERNAL STOP TRIGGER. IF AN "S" COMMAND, OR NO
COMMAND, HAS BEEN GIVEN, THE DIGITIZER WILL GO INTO THE SCOPE READOUT
MODE AFTER THE STOP TRIGGER. IF A "P" COMMAND IS GIVEN, THE PROGRAM WILL
READ OUT AND PLOT ON THE TERMINAL THE WAVEFORM CURRENTLY STORED
IN THE DIGITIZER. IF A "CONVERSION INITIATE" SIGNAL FROM THE COMPUTER
IS DESIRED, THEN AN "S" COMMAND MUST BE GIVEN. A "P" COMMAND MAY BE
GIVEN PRIOR TO THE EXTERNAL STOP TRIGGER, IN WHICH CASE THE WAVEFORM
OBTAINED IMMEDIATELY AFTER THE STOP TRIGGER WILL BE READ OUT AND
PLOTTED.

THE DATA, AS IT COMES FROM THE LECROY 2256AS TRANSIENT DIGITIZER, IS
NOT SUITABLE FOR AVERAGING DUE TO THE WAY IN WHICH NEGATIVE NUMBERS ARE
REPRESENTED. FOR INSTANCE, WHEN THE T.D. IS OFFSET SUCH THAT THE
DIGITIZING RANGE IS BETWEEN 0 AND -512 VOLTS, 0 VOLTS IS REPRESENTED
BY A DIGITAL 255. MANIPULATIONS OF AVERAGES ON THIS BASIS ARE AMBIGUOUS
BECAUSE OF AN ILL-DEFINED ZERO POINT. FOR THIS REASON, DATA FROM THE
T.D. IS CONVERTED USING THE FOLLOWING FORMULA:

\( \text{DATA} = \text{TDDATA} - \text{OFFSET} \) [NEW TD], OUR LECROY, WINTER 1981

WHERE "IDATA" IS THE DATA STORED IN "KEEPY", "TDDATA" IS THE DATA AS IT
COMES FROM THE T.D. AND "OFFSET" IS THE OFFSET INFORMATION FROM THE
TRANSIENT DIGITIZER. USING THE ABOVE EXAMPLE, THIS RESULTS IN THE
VOLTAGE RANGE BETWEEN 0 AND -512 VOLTS BEING REPRESENTED AS 0 TO -255
RATHER THAN AS 255 TO 0.

OFFSET INFORMATION IS ONLY OBTAINED FROM THE LECROY WHEN CALL ITDSET
IS EXECUTED.

LOCAL VARIABLE DEFINITIONS AND DATA

BYTE ANG(2), C(22), ID(40)
1 'R', 'N', 'Q', 'B', 'F', 'K', 'E', 'Z', 'O'/
DATA ANG/2*0/, NORMY/1/, IXOFF/0/, FACY/0, 0/
DATA FACX/0, 0/

GLOBAL VARIABLE DEFINITIONS AND DATA

BYTE FILNAM, DAIT, THYME
BYTE ESC
DATA ESC/"33/
COMMON/SKPDAT/NCHIG (NCHIG IS NO. CHANNELS SKIPPED. IF AMP NOT CN.
COMMON/ONEPIT/ONEPAR(6),GODDPT(341)
COMMON/TDATA/XKEEPY(341)
COMMON/TDUM/TDNUM, ITDPLG
COMMON/TDDATA/IFLAG, IFF(2), IDATN, KEEPY(1024)
COMMON/ARRAYS/X(341), Y(341), XKEEPY(341), MAXDAT
COMMON/PPINFO/IOFF, IPRETR, ISAMP, IATN, ISAM(8)/, IDIFLG, ISHOTS,
+ DAIT(9), THYME(8)
COMMON /SCLINF/XLIM, YLIM
COMMON /FNAME/FILENAME(16)
DIMENSION NSKIP(8), ORIGDT(341)
CH. SKIP FOR RISE TIME & SCAT LASER HV
DATA NSKIP/0, 0, 0, 0.2, .6, 10.25/
DATA X/341*0.0, Y/341*0.0, XKEEPY/341*0.0/
DATA XLIM/720.0, YLIM/360.0, XKEEPX/YKEEPX/341*0.0, MAXDAT/341/
DATA ISAN/0, 5000, 0, 1000, 500, 2, 100, 50/
DATA IDATN/341, 101FLS/O, /ISHOTS/0, /FITFLS/1, /
DATA IDNUM/16/
!==DEFAULT TD SLOT NUMBER

CALL SETERR(4, 255)
!KILL GOTO ERROR MESSAGE
CALL SETERR(5, 255)
!KILL INPUT CONVERSION ERR. MESS.
CALL ERRNS
!CLEAR THE ERROR BUFFERS

SAY HELLO TO THE USER AND FIND OUT THE TRANSIENT DIGITIZER

CALL DATE(DAIT)
CALL TIME(THYME)
CALL PAGE
CALL APAGE
WRITE(5, 1013) VER, DAIT, THYME
1013 FORMAT(2X, 'TRANSIENT DIGITIZER HANDLER'/32X,
! 'VERSION ', F4.2, '/', '23X, 9A1, 9X, 8A1///')

BEGIN BY SETTING UP THE TD PROPERLY

IF(IDSET(.), NE, 0) STOP 'TDHAND: COULD NOT PROTECT VECTOR'

NOW INITIALIZED TIME AND DATE AND GET A WAVEFORM.

104 CALL TIME(THYME)
CALL DATE(DAIT)
WRITE(5, 1102)
1102 FORMAT(' WARNING - TRANSIENT DIGITIZER IN WRONG SLOT OR'.,
! ' IN CONVERSION CYCLE.')</n
"E" - ENTER ID, SLITS, GAIN

WRITE(5, 1191)
1191 FORMAT(' LOOK AT THE 6-12-20 SWITCH ON THE TIMING LOGIC AND'.,
! ' PULSE ENERGY MONITOR BOX. CERTAIN SETTINGS ARE RECOMMENDED'.,
! ' IN ORDER TO FILL ENOUGH CHANNELS WITH BASELINE INFORMATION'.,
! ' YET NOT WASTE CHANNELS WITH TOO MUCH BASELINE. THE DELAY'.,
! ' SETTING IS RELATED TO THE NSEC/CHANNEL LE CROY SETTING IN'.,
! ' THE FOLLOWING WAY. '.,
! ' NSEC/CHANNEL MICROSECOND TIME DELAY SETTING '.,
! ' 50 6/'.,
! ' 100 12/'.,
! ' 200 12'/',
! ' 500 20/'.,
! ' 1000 20///')

WRITE(5, 6001) (ID(I), I=1, 40)
6000 FORMAT(' THE CURRENT ID IS ', 4OA1, //, ' DO YOU WISH TO CHANGE IT?'),
READ(5, 1004)ANS(1)
IF(ANS(1). NE, 'Y') GO TO 6003
WRITE(5, 6001)
6001 FORMAT(' ENTER THE ID IN 40 SPACES OR LESS'),
READ(5, 6002) (ID(I), I=1, 40)
6002 FORMAT(4OA1)
GO TO 1192
$003\hspace{1em}\text{WRITE}(5, 6004) \text{SLITEN, SLITEX}
$004\hspace{1em}\text{FORMAT}(\text{'\text{THE ENTRANCE SLIT WIDTH IS','F5.2', 'MM', '/',' THE EXIT SLIT', 'WIDTH IS ','F5.2', 'MM', '/',' DO YOU WISH TO CHANGE THEM?'}\text{')})
$005\hspace{1em}\text{READ}(5, 1004) \text{ANS}(1)
$006\hspace{1em}\text{IF(ANS(1).NE. 'Y') GO TO 6006}
$007\hspace{1em}\text{WRITE}(5, 6005)
$008\hspace{1em}\text{READ}(5, *) \text{SLITEN, SLITEX}
\hspace{1em}\text{GO TO 6003}
$009\hspace{1em}\text{WRITE}(5, 6007) \text{GAIN}
$010\hspace{1em}\text{ FORMAT(\text{' THE OP AMP GAIN IS ','F5.0', ' DO YOU WISH TO CHANGE IT?'}\text{')})
$011\hspace{1em}\text{READ}(5, 1004) \text{ANS}(1)
\hspace{1em}\text{IF(ANS(1).NE. 'Y') GO TO 1115}
$012\hspace{1em}\text{WRITE}(5, 6008)
$013\hspace{1em}\text{FORMAT(\text{' ENTER THE OP AMP GAIN IN F5.0 FORMAT'}\text{')})
\hspace{1em}\text{READ}(5, 1114) \text{GAIN}
$014\hspace{1em}\text{FORMAT(F5.0)}
\hspace{1em}\text{GO TO 6006}
$015\hspace{1em}\text{WRITE}(5, 1112) \text{FITFL0}
$016\hspace{1em}\text{ FORMAT(\text{' FITFL0 = ','F2.0', ' 1 = FIRST ORDER', ' 2 = SECOND ORDER', '/',' DO YOU WISH TO CHANGE THE VALUE OF FITFL0?'}\text{')})
\hspace{1em}\text{READ}(5, 1004) \text{ANS}(1)
\hspace{1em}\text{IF(ANS(1).NE. 'Y') GO TO 3}
\hspace{1em}\text{WRITE}(5, 1114)
$017\hspace{1em}\text{FORMAT(\text{' ENTER FITFL0'}\text{')})
\hspace{1em}\text{ACCEPT * , FITFL0}
\hspace{1em}\text{GO TO 1115}
$018\hspace{1em}3\hspace{1em}\text{CALL RCTRL0}
\hspace{1em}!!+001
\hspace{1em}\text{WRITE}(5, 1003)
$019\hspace{1em}1003\hspace{1em}\text{FORMAT(\text{' / TDH>\text{'}s\text{')})}
\hspace{1em}!!WRITE PROMPT
\hspace{1em}\text{READ}(5, 1004) \text{END=}3 \text{ANS}(1)
\hspace{1em}1004\hspace{1em}\text{FORMAT(A1)}
\hspace{1em}!!GET A COMMAND
\hspace{1em}\text{IF(ANS(1).NE. '32') GO TO 4}
\hspace{1em}\text{WRITE}(5, 1024) \text{VER}
$020\hspace{1em}1024\hspace{1em}\text{FORMAT(\text{' VER', 'F4.2')}
\hspace{1em}!!GO TO 3
$021\hspace{1em}4\hspace{1em}!!GO TO (100, 101, 116, 103, 104, 105, 106, 107, 108, 109, 110,
\hspace{1em}111, 112, 113, 114, 115, 116, 117, 118, 119, 120). \text{INDEX(C, ANS)}
$022\hspace{1em}\text{WRITE}(5, 1008)
$023\hspace{1em}1005\hspace{1em}\text{FORMAT(\text{' Illegal command. Reenter.'})}
\hspace{1em}\text{GO TO 3}
$024\hspace{1em}C\hspace{1em}"A" - ABORT COMMAND
$025\hspace{1em}C\hspace{1em}CALL ABORT
\hspace{1em}!!GO TO ABORT SUBROUTINE
$026\hspace{1em}C\hspace{1em}"W" - WRITE DATA TO A FILE
$027\hspace{1em}30\hspace{1em}CALL ERRNS( IERR, IUN)
\hspace{1em}!!+003
\hspace{1em}\text{WRITE}(5, 1027) \text{IERR, IUN}
\hspace{1em}!!+003
$028\hspace{1em}1027\hspace{1em}\text{FORMAT(\text{' File open error. Code= ','I3,2X, 'Unit= ','I3')\text{')})
\hspace{1em}!+003
\hspace{1em}\text{IF(IENAM() .LT. 0) GO TO 3}
\hspace{1em}\text{OPEN(UNIT=1) \text{NAME=FILNAM, TYPE='OLD', READONLY, DISP='SAVE',
\hspace{1em}FORM='UNFORMATTED', CARRIAGECONTROL='NONE',
\hspace{1em}BUFFERCOUNT=2, ERR=32)\text{')})
\hspace{1em}!!+003
\hspace{1em}\text{CLOSE(UNIT=1, DISP='SAVE')}
\hspace{1em}!!+003
\hspace{1em}\text{WRITE}(5, 1028)
$029\hspace{1em}1028\hspace{1em}\text{FORMAT(\text{' Overwriting existing file. ARE YOU SURE? '}\text{'s')})
\hspace{1em}!!+003
\hspace{1em}\text{READ(5, 1004, END=3) \text{ANS}(1)}
\hspace{1em}!!+003
\hspace{1em}\text{IF(ANS(1).NE. 'Y') GO TO 101}
\hspace{1em}!!+003
\hspace{1em}\text{OPEN(UNIT=1) \text{NAME=FILNAM, TYPE='NEW', FORM='UNFORMATTED',
\hspace{1em}CARRIAGECONTROL='NONE', DISP='SAVE', BUFFERCOUNT=2, ERR=30)
\hspace{1em}!!+003
\hspace{1em}\text{WRITE(1) ID}
\hspace{1em}\text{WRITE(1) DATE, THYME}
\hspace{1em}\text{WRITE(1) IDIFLO}
WRITE(1) ISHORT
WRITE(1) IOFFSET, IPRETR, ISAMP, IATTN
WRITE(1) GRIDT
WRITE(1) VI, GAIN, SLITEN, SLITEX

TYPE 9345

9345 FORMAT (' DO YOU WISH TO PLACE THE CURRENT VALUES OF ABSEX, 
AND THE FIRST ORDER PARAMETERS IN THIS NEW FILE? ') 
READ(5,1004,END=2) ANS
IF(ANNS(1).NE. 'Y')GO TO 34

9335 WRITE(1) ONEPAR(I), I=1,6
WRITE(1) ABSEX
WRITE(1) BSLE, JJ
GO TO 34

34 CONTINUE
CLOSE UNIT=1, DISP='SAVE')
GO TO 3

C
C "P" - COMPUTER READOUT AND PLOT
C
103 IF(ITDFLG.GT.0) GO TO 103
CALFLG=0
IDFLG=0
ISHOTS=1
MAXDAT=IDATN
NUM=IDATN-IOFFSET
CALL FPCONV
CALL SETX
CALL SETY(NORMY, GFAC, GMIN)
GFAC=0.01
GMIN=0.0
CALL PLT(IOFFSET, NUM)
GO TO 3

C
C "L" - PRINT OUT LABEL - THE FRONT PANEL SWITCH SETTINGS
C
105 WRITE(5,1008) DAIT, THYM, IDFLG, ISHORT, IOFFSET, IPRETR, ISAMP, IATTN
1008 FORMAT (' . , HAI, 5X, BAQ,/ ' Diff Flag=', '2/ ' I shots=', '4/ 
1 Offset=', '4/ ' Pretrig. samples=', '4/ ' Sampling ', 
1 period', '15/ ' Attenuator=', '13)
GO TO 3

C
C "X" - EXPAND THE X SCALE
C
106 WRITE(5,1009)
1009 FORMAT (' Factor=', 'S')
READ(5,1010,END=3) FACX
1010 FORMAT (E13.0)
IF(FACX.NE.0.0) GO TO 7
NUM=MAXDAT-IOFFSET
CALL SETX
CALL PLT(IOFFSET, NUM)
GO TO 3
7 IF(FACX.GT.0.0) GO TO 8
WRITE(5,1011)
1011 FORMAT (' Illegal Factor. Reenter. ') 
GO TO 106
8 CALL SCALE(X, MAXDAT, XLIM, FACX, NUM, GSCL, GLIM) 
1012 FORMAT (NUM=MINO(NUM, MAXDAT-IOFFSET)
CALL PLT(IOFFSET, NUM)
GO TO 3

C
C "H" - HELP - PRINT OUT DESCRIPTION OF COMMANDS
C
107 WRITE(5,1012)
1012 FORMAT(' The commands available are:
 ' 1 SX. ' A - Abort the program'/
 2 SX. ' B - Subtract background from signal, store result in a
 3 SX. ' C - Clear the screen'/
 4 SX. ' D - Obtain two summed waveforms and plot the difference'/
 5 SX. ' E - ENTER ID, SLITS, GAIN'/
 6 SX. ' F - Flip (swap) signal and background waveforms'/
 7 SX. ' G - List this text'/
 8 SX. ' H - Sum several shots and display the sum'/
 9 SX. ' I - Display Transient Digitizer Front panel settings'/
 10 SX. ' J - Check and change the normalization default flag'/
 11 SX. ' 0 - Display Transient Digitizer front panel settings'/
 12 SX. ' B - Read out the waveform currently stored in the
 13 SX. ' C - Initialize Transient Digitizer conversion cycle'/
 14 SX. ' D - Type out the raw data from the current waveform'/
 15 SX. ' E - Write out the waveform, etc. to a file on disk'/
 16 SX. ' F - Set the Y axis scale factor for the terminal plot'/
 17 SX. ' G - Check or change the Transient Digitizer slot number'/
 18 SX. ' H - Will cause return to "TDHi" prompt at all times' GO TO 3

C "I" - INTEGRATE OVER SEVERAL SHOTS AND DISPLAY

108 CALL TIME(THYME)
109 CALL DATE(DAIT)
110 CALL DACTO(ISH, VOLTN, GAIN)
111 WRITE(S, G) GAIN
112 IDIFLO=0
113 V1=VOLTN+1000.
114 IF V1>PMT W/SHUTTER OPEN IS IN MILLIVOLTS
115 IDIFLO=0
116 +003

TYPE 6666, IPF(1), IPF(2)

6666 FORMAT(' IPF(1)= ',07, ' IPF(2)= ',07)
15 MARK=0
DO 500 I=2, 1022, 3
500 MARK=MARK+1
TEMP3=DOUBLE(KEEPY(I-1)+KEEPY(I)+KEEPY(I+1))/3. *FLOAT(ISHSTD)
900 ORD(MARK)=TEMP3

5100 KKEEPY(MARK)=TEMP3
5B20 MAXDAT=IDATN
5C0 CALL FPDCMV
5C5 NSK=NSK(IPF(2), AND, '7')+1
5D0 NSK=NSK+2 = 2
5E0 TYPE = NSK
5F0 TYPE 6667, IQFF

6667 FORMAT(' IQFF= ',16)
8700 NCHIB=2000/(ISAMP+3) 'NO. CHANNELS TO IGNORE, IF AMP NOT ON
8800 CALL SETX
8900 CALL SETY(NORMY, QFAC, GMIN)
900 OAM=QFAC
9100 GMIN=GMIN
9200 NUM=IDATN=1XOFF

C FIND THE BASELINE AUTOMATICALLY AND THE MAX INTENSITY = MIN KEEPY.
9300 XMNX=0
9400 XITEM=1. E36
9500 SUM=0
9600 DO 8870 I=NCHIB+1, 130
8870 IF (XKEEPY(I) = XKEEPY(I)) GE 2*SGRT(FLOAT(ISHSTD)) GO TO 8870
8870 XITEM=AMIN(XKEEPY(I), XITEM)
8900 IF (XITEM EQ. XKEEPY(I)) XMNX=I

9870 CONTINUE
9900 DO 6500 I=NCHIB+1, IXMAX=NSK
5000 SUM=SUM+XKEEPY(I)
5000 I=NSK+1, NSK = NSK

5B2E=SUM/FLOAT((XMNX-NCHIB-NSK)) 'AVE UNSCALED XKEEPY UNITS
BSLE2=(BSLE1-OMPNI)*GFACTOR  'IN SCALED AVE XKEEPY UNITS.
XLITLE=XLTITLE  'IN UNSCALED AVE XKEEPY UNITS.
XCHFIL=BSLE1-XLTITLE  'NO. FILLED CHANNELS PER SHOT.
CALL PLT(IXOFF,NUNM)  'THE SUMMED KEEPY'S ARE PLOTTED.
WRITE(5,6501) XCHFIL,BSLE1,XLTITLE

6501 FORMAT(///////////,4(X,F10.2,' CHANNELS FULL PER DECAY CURVE'),
+ 4(X,'AVE BSLE=','F8.2,'AVE XINTMX=','F8.2))
GO TO 3

C      "C" - CLEAR THE SCREEN
109     CALL APRAGE
         CALL APAGE
         GO TO 3

C      "D" - TAKE THE DIFFERENCE BETWEEN TWO AVERAGED WAVEFORMS

110     WRITE(5,1016)
1016    FORMAT(' When you are ready for BACKGROUND sampling, type a',
1       '"CARRIAGE RETURN". ',/)
         READ(5,1004,END=3)
         CALL DATE(DT)
         CALL DACTOT(ISH, VOLTON, GAIN)
         ISHOTS=ISH
         MARK=0
         DO 5200 I=2,1022,3
         MARK=MARK+1
         TEMP3=FLOAT(KEEPY(I-1)+KEEPLY(I)+KEEPLY(I+1))/3.*FLOAT(ISHOTS)
         ORIGDT(MARK)=TEMP3
         KEEPY(MARK)=TEMP3
         CALL SWAP
         WRITE(5,1017)
1017    FORMAT(' When you are ready for SIGNAL sampling, type a',
1       '"CARRIAGE RETURN". ',/)
         READ(5,1004,END=3)
         CALL DACTOT(ISH, VOLTON, GAIN)
         ISHOTS=ISH
         V1=1.000  'VOLTON
         MARK=0
         DO 5300 I=1,1022,3
         MARK=MARK+1
         TEMP3=FLOAT(KEEPY(I-1)+KEEPLY(I)+KEEPLY(I+1))/3.*FLOAT(ISHOTS)
         ORIGDT(MARK)=TEMP3
         KEEPY(MARK)=TEMP3
         CONTINUE
         CALL BSUB
         DO 5530 I=1,MAXDAT
         5530     ORIGDT(I)=KEEPLY(I)
         GO TO 9920

C      "Y" - SET THE Y AXIS SCALE FACTOR

111     WRITE(5,1009)
         READ(5,1010,END=3) FACY
         IF(FACY.NE.0.0) GO TO 22
         NORMY=1
         FACY=0.0
         CALL SCALE(Y,MAXDAT,YLIM,FACY,1.,0SCL,0LIM)
         CALL PLT(IXOFF,NUNM)  'PLOT IT OUT
         GO TO 3
         22    IF(FACY.GT.0.0) GO TO 23
         WRITE(5,1011)
         GO TO 111
         23    IF(NORMY.NE.0) CALL SETY(O)
         NORMY=0
         CALL SCALE(Y,MAXDAT,YLIM,FACY,1.,0SCL,0LIM)
         CALL PLT(IXOFF,NUNM)
         GO TO 3
"T" - TYPE OUT SUMMED KEEPY DATA.

112 IF (IGETH(NCH1, NCH2, NE, 0)) GO TO 3
DO 1021 I=NCH1, NCH2
WRITE(1, 1021) I, KEEPY(I)
1021 FORMAT('Channel=', I4, 'Data=', I6)
IF (ITING(EG, '32')) GO TO 3
CONTINUE
GO TO 112

"R" - READ DATA FROM A FILE

31 CALL ERRNSR(IERR, IUN) ! ++003
WRITE(5, 1027) IERR, IUN ! ++003
113 IF (IGFNAM(N, L, 0)) GO TO 3
OPEN UNIT=1, NAME=FILNM, TYPE='OLD', READONLY, DISP='SAVE',
FORM='UNFORMATTED', CARRIAGECONTROL='NONE', ERR=31
WRITE(5, 1031)
1031 FORMAT('Read into background array? '),
READ(5, 1004) ANS(1)
IF (ANS(1), EQ, 'Y') CALL SWAP
READ(1, END=36, ERR=36) ID
READ(1, END=36, ERR=36) DAIT, THYME
READ(1, END=36, ERR=36) IDIFLG
READ(1, END=36, ERR=36) ISHTS
READ(1, END=36, ERR=36) IOFF, IPRETR, ISAMP, IATTN
READ(1, END=36, ERR=36) ORIGT
READ(1, END=36, ERR=36) VI, GAIN, SLITEN, SLITEX
CLOSE(UNIT=1, DISP='SAVE')
MAXDAT=IDATN
DO 5400 I=1, 341
5400 XKEEPY(I)=ORIGT(I)
GO TO 8700
36 CALL ERRNSR(IERR, IUN)
WRITE(5, 1027) IERR, IUN
GO TO 3

"N" - NORMALIZATION CHECK AND SET

114 IF (NORMY, EQ, '0') WRITE(5, *) 'Normalization -- OFF'
IF (NORMY, NE, '0') WRITE(5, *) 'Normalization -- ON'
WRITE(5, 1023)
1025 FORMAT('Enter normalization "ON" or "OFF" -- '),
READ(5, 1026, END=3) I
1026 FORMAT(A2)
IF (I, NE, 'ON') GO TO 24
NORMY=1
FACY=0
GO TO 3
24 IF (I, NE, 'OF') GO TO 114
NORMY=0
FACY=1
GO TO 3

"O" - CHECK AND CHANGE THE X AXIS OFFSET

118 WRITE(5, 1029) IXOFF
1029 FORMAT('Offset= ', I4, '/ Enter new offset= '),
READ(5, 1001, END=3) I
IF (I, GT, MAXDAT OR I, LT, 0) GO TO 115
IXOFF=I
CALL SCALE(X, MAXDAT, VI, IM, 1, 0, NNUM, GRC1, Q1 IM)
NUM=MINO(NUM, MAXDAT+IXOFF)
CALL PLT(IXOFF, NUM)
GO TO 3

C "G" - SUBTRACT BACKGROUND FROM SIGNAL
C
116	CALL 3GSUB
5500	GO 5900 I=1, MAXDAT
C
117	CALL SWAP
GO TO 8700

C "F" - FLIP (SWAP) THE SIGNAL AND BACKGROUND ARRAYS
C
C
C "Z" - CHANGE/CHECK THE DEFAULT TRANSIENT DIGITIZER SLOT POSITION
C
120	WRITE(5,1000) ITDNUM
1000	FORMAT(,'The current value for the slot number is ',I2/
**  + 'Enter the new value - 'S')
2	READ(5,1001,END=3) I
1001	FORMAT(213)
IF(I.EQ.0) GO TO 3
IF(I.GT.0 .AND. I.LT.22) GO TO 1
WRITE(5,1002)
1002	FORMAT('Illegal slot number. Reenter.')
GO TO 2
1	ITDNUM=I
IF(ITDSET().NE.0) STOP 'TDHAND: COULD NOT PROTECT VECTOR'
GO TO 3

C "K" - CALCULATE COMMAND
C
THE LIFETIME, FIRST ORDER PARAMETERS, AND CALCULATED DECAY
CURVE ARE FOUND. THE CALCULATED DECAY CURVE IS PLOTTED OVER
THE EXPERIMENTAL DECAY CURVE AND THE FIRST ORDER FIT PARAMETERS
AND LIFETIME ARE TYPED ON THE SCREEN BESIDE THE CURVES.
C
119	XISAMP=FLOAT(ISAMP)
119	XISHOT=FLOAT(IHOTS)
7205	TYPE 700, V1 ! V1 IS THE CURRENT PMT VOLTAGE.
700	FORMAT(,'THE CURRENT VALUE OF V1 IS ',F12.1, 'DO YOU WISH TO
** + CHANGE IT?')
READ(5,1004,END=3)ANS(1)
1004	FORMAT(213)
IF(ANS(1).EQ.'N') GO TO 7200
7202	TYPE 7202
7202	FORMAT(,'DO YOU WISH TO ENTER V1?')
READ(5,1004,END=3)ANS(1)
1004	FORMAT(213)
IF(ANS(1).NE.'Y')GO TO 3
7203	TYPE 7203
7203	FORMAT('V1 IN MILLIVOLTS IN F6.3 FORMAT IS> ')
READ(5,7204) V1
7204	FORMAT(F6.3)
GO TO 7205
C GET BASELINE, MAXIMUM INTENSITY, LEFT FIT LIMIT, AND RIGHT FIT LIMIT.
C DISPLAY BASELINE FOUND AUTOMATICALLY. FIND OUT IF IT IS OK.
7200	LBASEY=FIX(.94444444*BSLE2)+45 ! AUTFIT GRAPHICS UNITS.
TYPE 8851, +", ESC. LBASEY
8851	FORMAT(2A1,'n 90.',14,'o Z') ! MOVE CURSOR TO BSLE2
8853	TYPE 8853, +", ESC
8853	FORMAT(2A1,'*dk') ! TURN CURSOR ON.
8855	TYPE 8855
8852	FORMAT(1X,4OX, 'WOULD YOU LIKE TO ENTER A BASELINE',
** + /4OX, 'DIFFERENT FROM THIS?')
READ(5,1004)ANS(1)
1004	FORMAT(213)
IF(ANS(1).NE.'Y') GO TO 8854
85	TYPE 80
FORMAT(' POSITION THE CURSOR ON THE BASELINE. ') CALL TDCUR(IBASEX, IBASEY) TYPE 500. IBASEX, IBASEY SHOW CURSOR POSITION TO USER. BSEL=FLOAT(IBASEY) ! IN SCALED XKEEPY AVE UNITS.

86 FORMAT(' BASELINE=' 'F13.4') BSELKP=BSEL GO TO 6910

884 BSEL=BSEL2 ! IN AVE SCALED XKEEPY UNITS.

C DISPLAY DECAY CURVE MAXIMUM FOUND AUTOMATICALLY. FIND OUT IF OK.
6510 XLITL2=(XLITLE-GPMIN)*GPFA  ! SCALED AVE XKEEPY UNITS.

6520 XLITL2=IFIX(0.8444444*XLITL2)+0.5

6540 TYPE 604, '+', ESC, LITPOS ! MOVE CURSOR TO CURVE MAX.

6504 FORMAT(2A1,'=d 147','I4, ', 'a I') TYPE 8853, '+', ESC ! TURN ON CURSOR.

6502 TYPE 6502 FORMAT('//////', 40X, 'WOULD YOU LIKE TO ENTER A MAX', '///', 40X,

'DIFFERENT FROM THIS>?)') READ(5,1004) ANS(1)

6830 IF(ANS(1).NE. 'Y') GO TO 6503

690 FORMAT(' POSITION CURSOR ON MAXIMUM INTENSITY. ') CALL TDGCCUR(MAXX, MAXY)

6810 TYPE 900. MAXX, MAXY

6820 XINTM=FLOAT(MAXY) ! IN SCALED XKEEPY AVE UNITS.

6830 XINTM=XINTM IF(FITFLG.EQ. 2.) J=MAXX ! TZERO MUST BE TIME ZERO FOR 2ND ORDER FITS.

6503 GO TO 425

6910 XINTK=XLITL2 ! AVE SCALED XKEEPY UNITS.

6920 XINTK=XINTM

425 DO 5000 I=1, 341 GOODPT(I)=1.0 XKEEPY(I)=ORIGD(I)

5000 CONTINUE

5000 BSEL=BSELKP

5010 XINTM=XINTK IF(FITFLG.EQ. 2.) GO TO 60 ! LEFT LIMIT ALREADY ENTERED ABOVE.

5100 TYPE 420 ! ENTER LEFT FIT LIMIT.

5020 FORMAT(' POSITION CURSOR AT LEFT HAND FITTING LIMIT. ') CALL TDGCCUR(LIMXL, LIMYL)

5100 J= Liamx TYPE 300. LIMXL, LIMYL

5200 FORMAT(' XCOORDINATE= ', I4, '/ YCOORDINATE= ', I4)

5300 TYPE 95 ! ENTER RIGHT FIT LIMIT

5400 FORMAT(' POSITION CURSOR AT RIGHT HAND FITTING LIMIT. ') CALL TDGCCUR(LIRMXR, LIRMYR)

5500 J= LIRMX TYPE 300. LIRMXR, LIRMYR

5600 TYPE 66, '+', ESC ! TURN OF GRAPHICS CURSOR

66 FORMAT(2A1, '"dI')

C CONTINUE WITH FITTING.

6800 VOSCF=V/5AIN TYPE 2000. VOSCF 'VOLTAGE SCALING FACTOR IN MILLIVOLTS PER Y CHANNEL.

2000 FORMAT(' THE VOSCF IS ' 'F12.7') BSEL=BSEL/GPFA*GPMIN ! IN AVE XKEEPY UNITS

2010 XINTM=XINTM/GPFA*GPMIN ! IN AVE XKEEPY UNITS

2020 CALL SETERR(15.25) ! SUPPRESS SYSTEM CONTROL FOR ERROR LOG OF ZERO.

2030 ATEMP=(BSEL-XINTM)*VOSCF

2040 ABSMAX=ALOG10((V1/(V1-ATEMP)) ! MAXIMUM ABSORBANCE = ABSMAX

2050 NADPT=0 DO 279 I=1, JJ ! DO MATH FOR FIRST OR SECOND ORDER FIT.

2060 TEMP=BSEL-XKEEPY(I)

2070 IF(TEMP.LE.0.) GO TO 1200

2080
TEMP=TEMP+VOSOFT
TEMP=V/I/(VI-TEMP)
IF(FITFLG.EQ.1) GO TO 2002
XKEEP(I)=1./ALOG10(TEMP)
GO TO 275  ! SECOND ORDER DATA PREP DONE.
2002 XKEEP(I)=ALOG10(TEMP)  ! FIRST ORDER DATA PREP DONE.
CALL ERRNSG(IR, IU) ! SEE IF AN ERROR OCCURRED.
IF(IR.EQ.15) GO TO 8850 ! IF ERROR IS=LOG OF ZERO OCCURRED, GO TELL US
GO TO 275
1200 NADAPT=NADAPT+1
275 CONTINUE
XFIT=(J-J-1)*1
N=NFIT-NADAPT
CALL TOLTSG(N, J, JJ) ! DO THE FIRST ORDER FIT.
CALL CALCRT(VJ, VSCFT, J, JJ, BSLE, FITFLG) ! FIND CALCULATED FIT CURVE
CALL GSCF1(PPFAC, GMIN, J, JJ) ! SCALE THE CALCULATED DECAY CURVE.
CALL QPLOT(J, JJ) ! PLOT THE CALCULATED DECAY CURVE.
WRITE(5,9001) BSLE, J, JJ ! TYPE FITTING RESULTS ON TERMINAL.
9001 FORMAT(///,45X, 'BASILNLINE=', 'F8.2/', 45X, 'LEFT LIMIT= ', 'I4,' !
    'RIGHT LIMIT=' , 'I4')
WRITE(5,9200)  ABBMAX
9200 FORMAT(45X, 'THE MAXIMUM ABSORBANCE IS ', 'F7.4')
WRITE(5,9201) FITFLG
9201 FORMAT(45X, 'FITFLG = ', 'F2.0')
WRITE(5,9000) (ONEPAR(I), I=1,4)
9000 FORMAT(///, 45X, 'SLOPE= ', '1PE15.6/', 45X, 'SDSLOPE= ', '1PE15.6/', 45X,
        'INTERCEPT= ', '1PE15.6/', 45X, 'SDINT= ', '1PE15.6/', 45X, 'CORCO= ',
        '15.6/', 45X, 'LIFETIME= ', '1PE15.6/', 'MICROSEC')
IF(FITFLG.EQ.1) GO TO 9101
AZERO=1./ONEPAR(3)
HAFL1=ONEPAR(3)/(ONEPAR(1)*1000.)
WRITE(5,9203) AZERO, HAFL1
9203 FORMAT(45X, 'INITIAL ABSORBANCE BASED ON 2ND', '45X, 'ORDER',
        'INTERCEPT= ', 'F7.4/', 45X, '2ND ORDER HALFLIFE= ', '1PE15.6')
9101 TYPE 9105, NFIT, NADAPT
9105 FORMAT(\" THE FIT WAS ATTEMPTED ON \"I6, \" POINTS OF WHICH\" I6,
        \" WERE BAD POINTS. \")
9125 TYPE 9100
9100 FORMAT(\"S WOULD YOU LIKE TO REFIT THE DATA?\")
ACCEPT 1004, ANS(1)
IF(ANS(1).EQ.'Y') GO TO 425
DO 5501 I=1,341
5501 XKEEP(I)=XRIGHT(I)
GO TO 3
8850 WRITE(5,8860)
8860 FORMAT(\" THE ERROR LOG OF ZERO OCCURRED DURING DATA PREPARATION. \")
CALL SETHRR(15,1) ! REINSTATE SYSTEM CONTROL WHEN LOG(ZERO) OCCURS.
GO TO 3
STOP
END
SUBROUTINE APAGE

THE FUNCTION OF THIS SUBROUTINE IS TO CLEAR THE SCREEN OF THE
HP2648A GRAPHICS TERMINAL. ALPHANumerics ARE CLEARED BUT NOT
GRAPHS. THIS METHOD WAS BEGUN ON 11-MAY-81

BYTE ESC
DATA ESC/"33/

CLEARING THE SCREEN INVOLVES SHOWING THE NEXT PAGE OF MEMORY.

TYPE 1, '+' .ESC
FORMAT(2A1, 'U')
RETURN
END

AVBGSB.FOR

SUBROUTINE BGSUB

THIS SUBROUTINE SUBTRACTS THE "BACKGROUND" WAVEFORM FROM THE
"SIGNAL" WAVEFORM AND STORES THE RESULT IN THE "SIGNAL" WAVEFORM.

WRITTEN GREG LIVERMAN 14-FEB-80
++001 MODIFIED GREG LIVERMAN 21-FEB-80
- DELETED SOME INTEGER ARRAYS

BYTE DAIT, THYME
COMMON/RDATA/XKEEPY(341)
COMMON /TDDATA/IFLAG, IFP(2), IDATN, KEEPY(1024)
COMMON /ARRAYS/X(341), Y(341), XKEBOY(341), MAXDAT
COMMON /PINFO/IDFF, IFRETR, ISAMP, IATTN, ISAM(8), IDIFLG, ISHOTS,
+ DAIT(9), THYME(3)

TAKE THE DIFFERENCE

DO 1 I=1, MAXDAT
XKEEPY(I)=XKEEPY(I)-XKEBOY(I)
IDIFLG=1
CALL DATE(DAIT) !SET THE DIFFERENCE FLAG
CALL TIME(THYME) !GET NEW DATE AND
RETURN TO CALLING PROGRAM
RETURN
END
FUNCTION IGETCH(NLD,NHI)
C
IGETCH GETS TWO CHANNEL NUMBERS FROM THE USER TO BE USED AS
HIGH AND LOW LIMITS FOR SOME OTHER PROGRAM SECTION. THE CHANNEL
NUMBERS ARE RETURNED TO THE PROGRAM AS FOLLOWS.
NLD = LOWER CHANNEL NUMBER
NHI = HIGHER CHANNEL NUMBER
THE FUNCTION VALUE INDICATES IF THE USER HAS TYPED A "CTRL/Z"
AT THE TERMINAL:
IGETCH = 0 = NORMAL RETURN
IGETCH = -1 = CTRL/Z ENTERED AT TERMINAL

WRITTEN GREG LIVERMAN 29-JUL-80

COMMON /ARRAYS/X(341),Y(341),XKEEPY(341),MAXDAT

READ IN THE CHANNELS
IGETCH=0
WRITE(5,1000)
1000 FORMAT('Channel range (n1,n2): ')$
READ(5,1001,END=999) NLD,NHI
1001 FORMAT(25)
IF(NLD.LE.NHI) GO TO 1
I=NLD
NLD=NHI
NHI=I
1
IF(NLD.LE.0.OR.NLD.GT.1024) NLD=1
IF(NHI.LE.0.OR.NHI.GT.1024) NHI=1024
RETURN
C HANDLE CTRL/Z EXIT
C
999 IGETCH=-1
RETURN
END

SUBROUTINE GSETY(FAC,XMIN,L,M)
C FAC=SETY SCALING FACTOR FOR RAW KEEPY DATA.
C XMIN=MINIMUM XKEEPY VALUE FOR RAW DATA.
C COMMON/RDATA/XKEEPY(341)
FAC=ABS(FAC)
DO 100 I=L,M
TEMP=(XKEEPY(I)-XMIN)*FAC
100 XKEEPY(I)=TEMP
RETURN
END

AVGSET.FOR scales the decay curve values calculated
from the first or second order fit parameters.
SUBROUTINE OPLT(K1, K2)
COMMON/CNEPIT/CNEPAR(k), GOODPT(341)
COMMON/RDATA/GY(341)
BYTE ESC
DATA ESC/"33/"

CALL APAGE

FILL AUTOPLT MENU. USE DIFFERENT LINE TYPE THAN FOR THE RAW DATA.

N=(K2-K1)+1
TYPE 2, '+', ESC, N
FORMAT(2A1, 'a d 2h 1i 2j 1k 01 341m 0n 360o 50p 50q 80r 80s' +
+ '0t', '14', 'u Ov Ow z')

SLOW IT DOWN THREE SECONDS.
CALL WAIT(0.3, 0)

SET AUTOPLT TO ACCEPT DATA.
TYPE 4, '+', ESC
FORMAT(2A1, 'aaZ')

PLOT DATA
DATA IS SENT BY TYPING IT ON THE TERMINAL SCREEN. 2400 BAUD WORKS
WITH NO CHARACTERS SKIPPED.

DO 150 I=K1, K2
IF(GOODPT(I).EQ.0.0) GO TO 150
XI=FLOAT(I)
WRITE(5,100) XI, QY(I)
100 FORMAT(F3.0, X, F13.4)
IF(ITTNR().EQ."32") GO TO 50
TYPE 7, '+', ESC
7 FORMAT(2A1, 'K') ! CLEAR LINE ABOVE CURSOR.
TYPE 8, '+', ESC
8 FORMAT(2A1, 'A') ! MOVE CURSOR UP A LINE. NEXT POINT SAME PLACE.
150 CONTINUE

 TYPE 80, '+', ESC
80 FORMAT(2A1, 'a b z') ! TURN AUTOPLT OFF.
CALL APAGE
50 RETURN
END

AVGPIT.FOR plots the decay curve values calculated from the first or second order fit parameters.
AVLTSQ.FOR does first order least squares data analysis.

SUBROUTINE TOLTSG(N, J, JJ)
C N=NUMBER OF POINTS BEING FITTED
C J=LEFT LIMIT IN DATA ARRAY BEING FITTED.
C JJ=RIGHT LIMIT IN DATA ARRAY BEING FITTED.
C
C QNPAR(I)=SLOPE
C 2 STANDARD DEVIATION OF THE SLOPE
C 3 INTERCEPT
C 4 STANDARD DEVIATION OF THE INTERCEPT
C 5 CORRELATION COEFFICIENT
C 6 LIFETIME
C
COMMON/FPINFO/OFF, IPRETR, ISAMP, IATTN, ISAM(B), IDIFLG, ISHOTS,..
* DAIT(9), THYME(B)
COMMON/RDATA/XKEMHY(341)
COMMON/ONEFIT/ONEPAR(6), GOODPT(341)
BYTE ANS
XI=FLOAT(ISAMP)
S1=0.
S2=0.
S3=0.
S4=0.
S5=0.
DO 501 I=J, JJ
IF(GOODPT(I), EQ, 0.) GO TO 501
I1=I-J
XI1=XI
S1=S1+(XKEMHY(I)*XI1*XI1*3.)
S2=S2+XI1*XI1*3.
S3=S3+XKEMHY(I)
S4=S4+((XI1*XI1)*3.)*2
S5=S5+XKEMHY(I)*XKEMHY(I)
501 CONTINUE
TYPE 350. S1, S2, S3, S4, S5
550 FORMAT(' S1= ', 'E15.7/ ', 'S2= ', 'E15.7/ ', 'S3= ', 'E15.7/ ', 'S4= ', 'E15.7/ ', 'S5= ')
560 TYPE 360
550 FORMAT(' *TYPE A "Y" TO CONTINUE*')
ACCEPT S70. ANS
570 FORMAT(A1)
IF(ANS, NE, 'Y') GO TO 565
ZN=1.
DENOM=(Z3+Z4)-(S2*Z2)
ONEPAR(1)=((Z3+S1)-(S2+S3))/DENOM
ONEPAR(3)=((Z3-ONEPAR(1)*S2)/ZN)
RESID=0.0
DO 600 I=J, JJ
IF(GOODPT(I), EQ, 0.) GO TO 600
I1=I-J
XI1=XI
RESID=RESID+(XKEMHY(I)*XI1-(ONEPAR(3)-(ONEPAR(1)*XI1)*XI1)*XI1*3.)**2
600 CONTINUE
SIGN=SIGN/(ZN-2.)
ONEPAR(4)=SIGN((SIGN2*SIGN2)/DENOM)
ONEPAR(2)=SIGN((SIGN*SIGN)/DENOM)
S5=SIGN*ABS((S4+SIGN2*SIGN2)/ZN)/ZN-2.)
S6=SIGN*ABS((S5+SIGN2*SIGN2)/ZN)/ZN-2.)
ONEPAR(6)=(S5+SIGN2*SIGN2)/ZN)/ZN-1.)*S6*SY
ONEPAR(6)=ONEPAR(6)/1000. 'CONVERT FROM NANO TO MICRO SECONDS.'
RETURN
END
SUBROUTINE SWAP

THIS SUBROUTINE SWAPS THE "SIGNAL" AND "BACKGROUND" WAVEFORMS FOR USE IN "TOHAND".

WRITTEN GREG LIVERMAN 14-FEB-80
MODIFIED GREG LIVERMAN 21-FEB-80
- DELETED SOME INTEGER ARRAYS
- ADD "FPINFO" COMMON AND SWAPPING OF LABEL INFORMATION

BYTE DAITB(9), THYMES(8)
INTEGER*2 LABEL(6)
DATA LABEL/6*0/, DAITB/9*0/, THYMES/8*0/

BYTE DAIT, THYME
COMMON/RDATA/XKEEPY(341)
COMMON /TDATA/IFLAG, ITP(2), IDATN, KEEPY(1024)
COMMON /ARRAYS/X(341), Y(341), XEBOY(341), MAXDAT
COMMON /FPINFO/IOFF, IPRETR, ISAMP, IATTN, ISAM(8), IDIFLG, ISHTS.
+ DAIT(9), THYME(8)

SWAP THE TWO ARRAYS

DO 1 I=1, MAXDAT
   TEMP=XKEEPY(I)
   XKEEPY(I)=XEBGY(I)
   XEBGY(I)=TEMP
1 CONTINUE

SWAP LABEL INFORMATION

ITEM=IOFF
IOFF=LABEL(1)
LABEL(1)=ITEM

ITEM=IPRETR
IPRETR=LABEL(2)
LABEL(2)=ITEM

ITEM=ISAMP
ISAMP=LABEL(3)
LABEL(3)=ITEM

ITEM=IATTN
IATTN=LABEL(4)
LABEL(4)=ITEM

ITEM=IDIFLG
IDIFLG=LABEL(5)
LABEL(5)=ITEM

ITEM=ISHTS
ISHTS=LABEL(6)
LABEL(6)=ITEM

SWAP THE DATE AND TIME ALSO

DO 2 I=1, 9
   TEMP=DAIT(I)
   DAIT(I)=DAITR(I)
2 CONTINUE
DAITH(i)=ITEMP

DO 3 I=1,8
ITEMP=THYME(I)
THYME(I)=THYMEB(I)
THYMEB(I)=ITEMP
3 CONTINUE
RETURN TO CALLING PROGRAM
RETURN
END

AVSETX.FOR

SUBROUTINE SETX

THIS SUBROUTINE SETS THE X ARRAYS "IX" AND "X" TO THEIR INITIAL
VALUES (0, 1, 2, 3, ..., 340).

WRITTEN GREG LIVERMAN 15-JAN-80
++001 MODIFIED GREG LIVERMAN 14-FEB-80
- MODIFIED /ARRAYS/ TO INCLUDE "MAXDAT"
- MODIFIED /KEGY"
++002 MODIFIED GREG LIVERMAN 21-FEB-80
- DELETE SOME INTEGER ARRAYS

COMMON /ARRAYS/X(J341), Y(J341), XKEGY(J341), MAXDAT

SET THE ARRAYS

DO 1 I=1, MAXDAT
X(I)=FLOAT(I-1)
1 CONTINUE
RETURN
END
SUBROUTINE COOL(dpmt, dopa, gain)
C DESIGNED FOR CHOPPED LIGHT. USES CAMAC MULTIPLE ACTION FUNCTION.
COMMON/SUBCOM/DACAD, ADDR, OR3AD, F, A
INTEGER*2 DACAD, ADDR, OR3AD, F(3), A(3), DPMT(3), DOPA(3), CB(3)
LOGICAL*1 GA(3)
CB(1)=0
C NEXT ROUTE READS PMT AND OP AMP OUTPUT ON SUCCESSIVE CHOPPER
C LIGHT PULSES.
C
19 CALL CSFA(F, A, DPMT, GA, C3) ! SET TO READ PMT VOLTA GE (CH. 1)
C IF ( NOT.G) GO TO 19 ! WAIT FOR CHOPPER ALIGNMENT
CALL CSFA(F, A, DOPA, GA, C3) ! SET TO READ OP AMP VOLTA GE
22 CALL CSFA(F, A, ADDR, IOUT, G) ! READ OP AMP OUTPUT (CH. 0)
IF ( NOT.G) GO TO 22 ! CYCLE UNTIL CHOPPER ALIGNED
IF (IOUT.LE. 2047) GO TO 100 ! FOR NEGATIVE VOLTS
IOUT = IOUT - 4095
100 OPOUTA = (FLOA T(IOUT))/400.0
PHOTOA = (FLOA T(IPHOT))/400.0 ! CONVERTS ANSWER TO VOLTS
TYPE 200, OPOUTA, PHOTA
200 FORMAT(1X, 'OP=' ', F7.3, ' PMT=' ', F7.3) ! TYPES VALUES BEFORE NULLING
J=0
501 IADJ = IFIX((FLOA T(IPHOT+1995))*.1.024) ! MAKES OFFSET V = PMT V
502 J=J+1
CALL CSFA(F, A, DACAD, IADJ, G) ! WRITES OFFSET VOLTAGE TO DA/12
CALL CSFA(F, A, DPMT, GA, C3) ! SET TO READ PMT VOLTA GE
21 CALL CSFA(F, A, ADDR, IPHOT, G) ! READS OUT PMT
IF ( NOT.G) GO TO 21 ! CYCLES UNTIL FLIP FLOP RESET
CALL CSFA(F, A, DOPA, GA, C3) ! READS OUT OP AMP OUTPUT
33 CALL CSFA(F, A, ADDR, IOUT, G) ! READS OP AMP OUTPUT
IF ( NOT.G) GO TO 23 ! CYCLE UNTIL FLIP FLOP RESET
IF (IOUT.LE. 2047) GO TO 300
IOUT = IOUT - 4095
300 OPOUTA = (FLOA T(IOUT))/400.0
PHOTOA = (FLOA T(IPHOT))/400.0
7 TYPE 400, OPOUTA, PHOTA
400 FORMAT(1X, 'OP=' ', F7.3, ' PMT=' ', F7.3)
IF (J.GE.6) GO TO 10 ! ONLY GETS 6 TRIES TO NULL
IF (OPOUTA.LE.-0.11) GO TO 501
IF (OPOUTA.GE.0.1) GO TO 501
IF (OPOUTA.GE.-0.02) AND (OPOUTA.LE.0.02) GO TO 10
CORMAT = (OPOUTA/GAIN) + 4.095 ! CORRECTS IADJ IF WE'RE CLOSE
IADJ = IADJ + IFIX(CORMAT)
GO TO 502
10 RETURN
END
SUBROUTINE PLT(IOFSET, N)

N=NUMBER OF POINTS

THIS SUBROUTINE PLOTS AN X AND Y ARRAY ON THE HP2648A GRAPHICS TERMINAL BY INVOKING THE GRAPHING CAPABILITIES OF ITS AUTOPLLOT MODE.

COMMON /ARRAYS/X(341), Y(341), XXEDGY(341), MAXDAT
COMMON/SKIPDAT/NCHIG ! CH. TO IGNORE. OP AMP NOT NO YET.
BYTE ESC
DATA ESC/"33/"

CLEAR GRAPHICS MEMORY

8000 TYPE 1, ' + ', ESC
FORMAT(2A1, '4A')

FILL THE AUTOPLLOT MENU THEN DRAW AXES

10 TYPE 2, ' + ', ESC, N=NCHIG+1
FORMAT(2A1, 'a d 2h 11 2j 9k 0l 341m 0n 360o 50p 90q 80r 80s
Ot', 14, 'u 0v 0w c z')

SLOW THINGS DOWN A LITTLE.

CALL WAIT(0,3.0)
TYPE 5, ' + ', ESC
FORMAT(2A1, 'U') ! NEXT PAGE, PLEASE.
TYPE 4, ' + ', ESC
FORMAT(2A1, 'aaaZ') ! TURN AUTOPLLOT ON.
TYPE 6, ' + ', ESC
FORMAT(2A1, 'B') ! NEXT LINE, PLEASE.

PLOT DATA! DATA IS SENT BY TYPING IT ON THE TERMINAL SCREEN.
2400 baud works with no characters skipped.

J=IOFSET+1+N
DO 150 I=IOFSET+NCHIG+1, J, 3
WRITE(5,100) X(I), Y(I)
100 FORMAT(F8.0, X, F13.4)
IF(ITITINR()) EQ. "32") GO TO 50
TYPE 7, ' + ', ESC
7 FORMAT(2A1, 'K') ! CLEAR LINE ABOVE CURSOR.
TYPE 8, ' + ', ESC
FORMAT(2A1, 'A') ! MOVE CURSOR UP A LINE. WRITE NEXT POINT IS SAME SPOT.
8 CONTINUE
TYPE 80, ' + ', ESC
9 FORMAT(2A1, 'a b Z') ! TURN AUTOPLLOT OFF.
RETURN
END
SUBROUTINE SCALE(RARRY, N, RLIM, RSCL, NUM, QSCL, QLIM)

MODIFIED 9-27-81 BY T. WOODS TO IGNORE DATA WHEN OP AMP IS NOT TURNED ON

THIS SUBROUTINE SCALES AND/OR NORMALIZES A REAL ARRAY, "RARRY", STORING THE RESULT BOTH IN "RARRY" AND IN AN INTEGER ARRAY, "IARRY".

ONLY SCALING IS DONE IF "RSCL" IS POSITIVE. IF "RSCL" IS NEGATIVE THEN THE ARRAY IS ADJUSTED SO THAT IT IS POSITIVE AFTER FINDING THE MAXIMUM AND MINIMUM AND THEN IT IS SCALED USING THE ABSOLUTE VALUE OF "RSCL". IF "RSCL" IS ZERO, THEN THE ARRAY IS AUTOMATICALLY
NORMALIZED AND SCALED TO THE LIMIT SPECIFIED IN "RLIM"

NOTE THAT ALL VARIABLES EXCEPT "N" AND "RLIM" ARE MODIFIED BY THIS
ROUTINE!!

COMMON/SPDAT/NCHIG !NCHIG IS CHANNELS SKIPPED. OP AMP NOT ON.
                  DIMENSION RARRY(N)

SEE IF WE NORMALIZE OR JUST SCALE
RMIN=0.0 !MAKE SURE RMIN IS DEFINED
IF(RSCL.GT.0.0) GO TO 1

FIND THE MINIMUM AND MAXIMUM OF THE ARRAY
RMAX=RARRY(1)
RMIN=RMAX
DO 2 I=NCHIG+1,N
    RMAX=MAX(RMAX,RARRY(I))
    RMIN=MIN(RMIN,RARRY(I))
2 CONTINUE

FIND OUT IF WE COMPUTE OUR OWN SCALE FACTOR
IF(RSCL.LT.0.0) GO TO 1

COMPUTE THE SCALE FACTOR
    DIF=RMAX-RMIN
    RSCL=1.0
    IF(DIF.NE.0.0) RSCL=RLIM/DIF
    QSCL=RSCL
    QLIM=RMIN

MULTIPLY ARRAY BY SCALE FACTOR AND FORM INTEGER RESULT
NUM=0
    RSCL=ABS(RSCL)
    DO 3 I=NCHIG+1,N
        RARRY(I)=INT((RARRY(I)-RMIN)*RSCL)
        IF(RARRY(I).LT.RLIM) NUM=I
    3 CONTINUE

RETURN
END
SUBROUTINE SETY(NORM, GFA, GMIN)

THIS SUBROUTINE SETS THE Y ARRAYS "IY" AND "Y" TO THEIR INITIAL
VALUES. THE INITIAL VALUE FOR THESE IS DERIVED FROM "KEEPY", THE MASTER
COPY OF THE DATA FROM THE TRANSIENT DIGITIZER OR AN EXISTING FILE.
"KEEPY" IS SCALLED TO AND NORMALIZED USING "YLim" ONLY IF "NORM" IS
NON-ZERO.

WRITTEN GREG LIVERMAN 15-JAN-79

MODIFIED T. WOODS 4-SEPT-81 TO SKIP DATA BEFORE OP AMP IS ON AND TO
HANDLE AVERAGED KEEPY DATA LOADED INTO XKEEPY.
COMMON /ARRAYS/X(341), Y(341), XKEEPY(341), MAXDAT
COMMON/RDATA/XKEEPY(341)
COMMON/KEEPDAT/NCHIQ ! CH. TO SKIP, OP AMP NOT ON YET.
COMMON /TDATA/IFLAG, IFP(2), IDATN, KEEPY(1024)
COMMON /SCLINF/XLIM, YLIM

LOAD "XKEEPY" INTO "Y"

DO 1 I=NCHIQ+1, MAXDAT
  Y(I)=XKEEPY(I)
1  SCALE AND NORMALIZE

  SCL=0.0
  IF(NORM, EQ, 0) SCL=-1.0
  CALL SCALE(Y, MAXDAT, YLIM, SCL, I, GSCL, GLIM)
  GFA=GSCL
  GMIN=GLIM

1000 RETURN
END

SUBROUTINE CALCFT(V1, VOSCF, JJ, SE, FITFLG)

THIS SUBROUTINE CALCULATES THE FIRST ORDER DECAY CURVE FROM THE
FIRST ORDER FIT PARAMETERS.
COMMON/RDATA/XKEEPY(341)
COMMON/ONEFIT/ONEPAR(6), QOODPT(341)
COMMON/FINFO/IDFF, IPRETR, ISAMP, IATTN, ISAM(5), IDIFLG, ISHOTS,
  DALT(9), THYME(8)
  XISAMP=FLOAT(ISAMP)
  DO 900 JJ=1, SE
    IF(QOODPT(JJ), EQ, 0) GO TO 800
    I=I-J
    XI=1
    XKEEPY(I)=ONEPAR(3)+ONEPAR(1)*XI*XISAMP+3.
    IF(FITFLG, EQ, 2) GO TO 900
    TEMP=EXP(XKEEPY(I))
    GO TO 810
  810 TEMP=1./XKEEPY(I)
  820 TEMP=10.**TEMP
   TEMP=TEMP/V1
   TEMP=1./TEMP
   TEMP=1.*TEMP
   XKEEPY(I)=(SE*SE-VOSCF-VOSCF)/VOSCF
900 CONTINUE
RETURN
END
This is a program to handle the LeCroy 2236 Transient Digitizer versions "A" and "S". Conversions may be initiated by a call to the routine:

CALL ITD(IDBUF, IFPBUF, NCONV, NWORDS)
OR
IERR = ITD(IDBUF, IFPBUF, NCONV, NWORDS)

Where:

IDBUF - Buffer to receive the data from the transient digitizer. This buffer must be an INTEGER*2 array "NWORDS" long. The data in this array is the sum of "NCONV" conversions and is formatted according to the description given below before the "TDINT" routine.

IFPBUF - Buffer to receive the front panel information. It must be an INTEGER*2 variable two words long. The front panel information is placed as follows:

IFPBUF(1) - Attenuator setting ("S" model only, non-"S" model gives 0)
IFPBUF(2) - Other front panel settings and offset information.

The information in "IFPBUF" is formatted according to the description in the 2236 manual.

NCONV - The number of waveforms to be summed together.
NWORDS - The number of words to be read out of the 2236 for each conversion. This variable must be an INTEGER*2 and can have a maximum value of 1024.

IERR - Error code: IERR = 0 - Normal return
IERR = -1 - Unit in wrong slot

The calling program MUST perform a call to the setup routine, "ITDSSET", BEFORE calling "ITD". This routine initializes the interrupt vector and calculates the addresses used by "ITD" and the interrupt service routine "TDINT". The calling format for "ITDSSET" is:

CALL ITDSSET
OR
IERR = ITDSSET()

Where:

IERR - Error code: IERR = 0 - Normal return
IERR = -1 - Could not protect vector, no action taken.

The calling program MUST have a common block defined as follows:

COMMON /TDCOM/ ITDNUM, ITDFLG

Where:

ITDNUM - Slot number of transient digitizer (must be initialized prior to the call to "ITDSSET") and must be an INTEGER*2 variable.

ITDFLG - An INTEGER*2 variable which serves as a communication link between the main program and the interrupt routine:

ITDFLG = 0 - Data acquisition is complete and the data in "IDBUF" is valid.
ITDFLG = 1 - Data acquisition is in progress, the data in "IDBUF" is not valid.
ITDBUF = -1 - The main program may set "ITDBUF" to -1 if an immediate abort of the data acquisition is desired. The data is valid after the abort and the actual number of conversions performed will be deposited in "NCONV". Also, "ITDFLAG" will be set to 0.

The basic operation of this routine is described here. The program initiates a conversion cycle on the LeCroy 2256. When an external trigger stops the conversion, the 2256 interrupts the computer and the data is "Added" out of the 2256 into the user's buffer. When the preset number of waveforms has been acquired, then this routine obtains the offset and front panel information and modifies the data in the user's buffer according to the scheme described below. The communication flag, "ITDFLAG" is then cleared to signal the user that the process is complete.

The setup routine, "ITDSET" determines the type of 2256 that is being used ("A" and/or "S"). If it is an "A" model, the OFFSET information is digitized when "ITDSET" is called. It should be noted that if the user changes the OFFSET after "ITDSET" is called, then a second call must be made to that routine to re-digitize the OFFSET.

NOTE ABOUT INTERRUPT PRIORITY

The interrupt service routine takes about 15 msec (on LSI-11/2) to obtain all 1024 points from the 2256. During the last acquisition, it is approximately 30 msec since the user's array must be processed twice to accommodate the OFFSET information. If the processor priority is kept above 3 for this period of time, degradation of overall system performance may result (note that the line time clock interrupts every 10 msec). Running the interrupt service routine at a priority of 3 or less is acceptable with respect to the LeCroy or other CAMAC interrupts since the routine turns off the CAMAC interrupts immediately upon entry. However, as noted in the RT-11 manuals, lowering the interrupt below 4 may cause reentrancy problems with other interrupt service routines that may have been interrupted by this one.

Users who wish to operate the LeCroy at acquisition rates approaching the maximum (30-60 Hz) should observe the "CARRY OUT TRIGGER" (COT) while running this program under the actual computer load conditions to be used in the experiment. The falling edge of the COT marks the end of the conversion cycle and the rising edge marks the readiness of the LeCroy to accept another STOP TRIGGER.

Written Greg Liverman 22 Mar 80

++001 Modified Greg Liverman 29 Jan 81
- Revise the preface
- Add code to handle "A" model
- Clean up interrupt service routine and improve throughput

PAGE

============================================================================
SITL SYMBOLS: MCALL, COMMON BLOCK

Define some symbols

IIF NDF CMCBAS, CMCBAS = 170000
IIF NDF CMVECM, CMVECM = 400
CMCSR = CMCSR + 1400
TDPRI = 4

T.D. INTERRUPT PRIORITY


MCALL directive

MCALL INTEN., PROTECT

/TDCOM/ Common Block

PSECT TDCOM.RW.D, G3L.REL.OVR
ITDNUM: .BLKW 1
ITDFLO: .BLKW 1

Define normal PSECT

PSECT ITD.RW.I, LCL.REL, CON

PAGE

===========================================================================
SBITL ITDSET
===========================================================================

ITDSET:

CLR ITDFLO          ;CLEAR THE FLAG
MOV ITDNUM,R1      ;GET THE SLOT NUMBER
ASH #2,R1          ;START TO CALC. A VECTOR
ADD #CMVEC,R1      ;ADD IN THE VECTOR BASE
PROTECT #AREA,R1    ;PROTECT THE VECTOR
SCS 1               ;EXIT WITH ERROR IF WE CAN'T PROT.
MOV #TDINT,(R1)+    ;LOAD THEVECTOR
MOV #340,(R1)       ;ALSO THE PSW
MOV ITDNUM,R1      ;GET ANOTHER COPY OF SLOT NUMBER
MUL #40,R1          ;START TO CALC. AN ADDRESS
ADD #CMBSAS,R1      ;ADD IN THE BASE
MOV R1,TDA0D        ;AND SAVE IT FOR LATER

Note that the address in TDA0D is the address of the LaCroy for
subaddress 0.  No others need be calculated since all commands to the
2256 are to subaddress 0.

CLR CONFIO          ;CLEAR CONFIGURATION WORD
BIC #7,#CMCSR       ;GET READY FOR CAPAC ACTION
MOV (R1).RO         ;DO FO AT THE LECROY
BIT #100,#CMCSR     ;SEE IF WE GET AN "X"
BEQ 2               ;IF NOT, IT'S NOT AN "S"
BIS #1,CONFIO       ;GET OUR "S" BIT
2:                    
BIS #4000,#CMCSR     ;GET READY FOR CONTROL CODE
MOVB #27,(R1)       ;DO AN F27
BIT #100,#CMCSR     ;SEE IF WE GET AN "X"
BEQ 3               ;IF NOT, IT'S NOT AN "A"
BIS #2,CONFIO       ;GET OUR "A" BIT
DIC #4000,#CMCSR     ;GET READY FOR F1
INC #CMCSR          ;AND ALSO SET A BIT
4:                    
MOV (R1).RO         ;DO AN F1
BIT #200,#CMCSR     ;CHECK THE Q BIT
BEQ 4               ;AND WAIT 'TIL IT'S SET

After this section the OFFSET digitization for the model "A" is
complete.

3:                    
BIC #4000,#CMCSR     ;MAKE SURE NREAD BIT IS OFF
CLR RO                ;CLEAR ERROR CODE
RETURN                ;AND GO BACK

Next section is error return if we couldn't protect the vectors.
1$: MOV #-1,RO  ; SET THE ERROR CODE
RETURN     ; AND GO BACK

PAGE

==============================================
SSTTL TDINT
==============================================

ITD:
TST ITDFLG ; SEE IF THE LAST ONE IS THROUGH
BNE ITD    ; WAIT IF IT'S NOT EQUAL TO ZERO
TST (RS)+ ; INCREMENT RS BY TWO
MOV (RS),BUFPT ; GET THE BUFFER ADDRESS
MOV (RS)+,RO ; INTO RO ALSO
MOV (RS)+.FPPT ; GET FRONT PANEL BUFFER ADDRESS
MOV @RS,NCONV ; GET NUMBER OF CONVERSIONS
MOV @RS-.NCONV2 ; IN TWO PLACES
MOV @RS+.NWORDS ; GET NUMBER OF WORDS ALSO
MOV @RS+.R1 ; ALSO INTO R1
1$: CLR (RO)+ ; CLEAR THE USER'S BUFFER
SBS R1,1$ ; DO IT ALL
BIS #4000,@CMCSR ; SET NO READ BIT
MOV B #9, @TDADD ; DO F9
BIT #100,@CMCSR ; CHECK "X" BIT
SEQ 2$ ; ERROR IF NOT SET
MOV B #26, @TDADD ; ENABLE LECROY LAM
BIC #4000,@CMCSR ; TURN OFF NO READ BIT
MOV #1, ITDFLG ; SET FLAG - MEN AT WORK!
CLR RO ; CLEAR THE ERROR CODE
BIS #4000,@CMCSR ; MAKE SURE INTERRUPTS ARE ON
RETURN ; AND GO HOME

The next section handles the error code if the unit is in the
wrong slot.

2$: BIC #4000,@CMCSR ; CLEAR NO READ BIT
MOV W-1,RO ; SET ERROR CODE
RETURN ; GO TELL THEM THE BAD NEWS

PAGE

==============================================
SSTTL ITD
==============================================

This is the interrupt service routine. The data as it comes from the
LeCroy is unsatisfactory for averaging unless the OFFSET information
is included. This program leaves the data in the user's buffer that
has been modified according to the following:

- UDATA = TDDATA + (OFFSET - 255.)  [For 2256]
- UDATA = TDDATA - OFFSET  [For 2256A]

Where:
- UDATA - Data in user's buffer
- TDDATA - Raw data from the transient digitizer
- OFFSET - Offset information from transient digitizer

TDINT:
BIC #4000,@CMCSR ; TURN OFF CAMAC INTERRUPTS
.LEN TDPI ; LET RT-11 KNOW WE ARE HERE
MOV @CMCSR,-(SP) ; SAVE THE CAMAC CSR ON THE STACK
BIS #4000,(SP) ; SET INTERRUPT BIT ON THE STACK COPY
MOV @CMCSR+2,-(SP) ; SAVE HIGH DATA REG. ON STACK
MOV R1,-(SP) ; SAVE R1 ON THE STACK
TST ITDFLG ; SEE IF WE HAVE TO ABORT
BMI 1$ ; IF SO, WE GO DO IT
Next section is normal readout of data from the LeCroy.

MOV TDADD, R1    ; GET THE ADDRESS HANDY
MOV NWORDS, R4    ; AND A LOOP COUNTER
MOV BUFPTR, R5   ; AND THE BUFFER ADDRESS
SIC #4007, @MCCSR  ; CLEAR NO READ AND F CODE BITS
SIS #2, @MCCSR    ; SET UP FOR F2
ADD (R1), (R5)+   ; ADD THE DATA OUT OF THE LECROY
SOS R4, 26        ; LOOP THROUGH ALL THE DATA
DEC NCONV         ; DEC THE CONVERSION COUNTER
BLE 1s             ; WHEN ZERO, WE'RE ALL DONE
SIS #4000, @MCCSR  ; SET THE NO READ BIT
MOVB #9, (R1)     ; RESET THE LECROY (F9)
MOVB #26, (R1)    ; ENABLE LAM (F26)
BR 3s             ; AND GO TO EXIT CODE

This next section is executed only after the preset number of
waveforms have been obtained. Here the front panel info (incl. offset)
is obtained and placed in the proper place. The user's data is also
re-evaluated using the offset info.

1s:  MOV FPPT, R5       ; GET FRONT PANEL BUFFER ADDRESS
BIC #$7, @MCCSR       ; PREPARE FOR NEW F CODE
BIT $11, CONFIG      ; CHECK THE CONFIGURATION
BEQ 4s              ; WE DON'T HAVE TO READ IT IF NOT "S"
MOV (R1), (R5)+      ; DO AN FO (GET ATTENUATOR)
BR 5s            ; BRANCH AROUND NEXT STUFF
4s:  CLR (R5)+        ; THIS IS FOR NON-"S" MODEL
INC @MCCSR          ; PREPARE FOR F1
MOV (R1), (R5)       ; GET OTHER INFO (INCL. OFFSET)
MOV (R5), R1         ; GET IT WHERE WE CAN MANIPULATE IT
SIC #$77, R1        ; DELETE ALL EXCEPT OFFSET
ASH #6, R1          ; SHIFT OFFSET INTO POSITION
BIT $22, CONFIG     ; CHECK FOR "A" MODEL
BNE 10s            ; DON'T DO NEXT STUFF FOR "A" MODEL
SUB #255, .R1       ; SUBTRACT 255.
NEG R1              ; NEG THE RESULT SO WE DO AN "ADD" LATER
10s: MUL NCONV2, R1   ; MULTIPLY BY NUMBER OF CONVERSIONS
MOV NWORDS, R4      ; SET UP LOOP COUNTER
MOV BUFPTR, R5      ; GET THE BUFFER ADDRESS
SUB R1, (R5)+      ; "ADD" IN THE OFFSET TO USER'S DATA
SOS R4, 6s        ; GO THROUGH WHOLE BUFFER
CLR ITDFLAG        ; CLEAR THE FLAG
SIS #4000, @MCCSR  ; SET UP FOR F24
MOVB #24, TDADD     ; DO F24 (DISABLE LAM)
3s:  MOV (SP)+, R1    ; REPLACE R1
MOV (SP)+, @MCCSR+2 ; AND THE HIGH DATA WORD
MOV (SP)+, @MCCSR   ; AND THE CAMAC CSR (WITH IE BIT SET)
RETURN

PAGE

=================================================================
SITTL VARIABLE STORAGE AREA
=================================================================

AREA:  BLK4 3
TDADD:  BLK4 1
BUFPTR: BLK4 1
FPPT:   BLK4 1
NCONV:  R1 1
NCONV2: BLK4 1
NWORDS: BLK4 1
CONFIG: BLK4 1

END

THAT'S ALL FOLKS!!!
SUBROUTINE PAGE

THE FUNCTION OF THIS SUBROUTINE IS TO CLEAR THE SCREEN OF
THE HP2646A GRAPHICS TERMINAL. GRAPHICS ARE CLEARED BUT
NOT ALPHANUMERIC.

BYTE ESC
DATA ESC/"33/
TYPE 1. '+' ESC
FORMAT(2A1, '*dA')
RETURN
END

TDABOR.FOR

SUBROUTINE ABORT

THIS SUBROUTINE PROVIDES CONVENIENT COMMON EXIT CODE

WRITTEN GREG LIVERMAN 15-JAN-80

++001 MODIFIED GREG LIVERMAN 10-MAR-80
- REMOVE CALLS TO INTERFACE HANDLER
  ROUTINES

++002 MODIFIED GREG LIVERMAN 21-MAR-80
- REMOVE CALL TO TDKILL, REPLACE WITH
  CODE COMPATIBLE WITH "ITD.MAC", THE NEW
  TRANS. DIG. HANDLER.

COMMON /TCOM/ITDNUM, ITDFLG

MAIN CODE

CALL PAGE
ITDFLG=-1
STOP 'TRANSIENT DIGITIZER HANDLER'
END
SUBROUTINE FPConv

SUBROUTINE CONVERTS THE FRONT PANEL INFORMATION INTO THE FORM USED IN THE PROGRAM. IT DECODES IT FROM TWO WORDS PASSED FROM THE TRANSIENT DIGITIZER IN "IFP" THIS ROUTINE PROVIDES CONVENIENT CONVERSION FUNCTION SO MODULAR PROGRAM DEVELOPMENT MAY BE REALIZED.

WRITTEN GREG LIVERMAN 15-JAN-90
MODIFIED GREG LIVERMAN 21-FEB-80
- ADD VARIABLES TO "FPINFO"

BYTE DAIT, THYME
COMMON /TDATA/IIFLAG, IFP(2), IDATN, KEEPY(1024)
COMMON /FPINFO/I OFFSET, IPRETR, ISAMP, IATTN, ISAM(8), IDIFIO, ISHOTS,
* DAIT(9), THYME(8)

DECODE THE FRONT PANEL INFO.

IOFFSET=IFP(2) AND "177700/64
IPRETR=IFP(2) AND "70"X4
ISAMP=ISAM(IFP(2) AND "7"X1)
IATTN=IFP(1)/8+100 MOD(IFP(1), 8)
IF(IATTN.EQ.4) IATTN=5
RETURN
END

SUBROUTINE TDGCUR(NLX, NLY)

THIS SUBROUTINE ALLOWS YOU TO POSITION THE GRAPHICS CURSOR ON THE 2640A GRAPHICS TERMINAL AND RETURN TO THE MAIN PROGRAM THE COORDINATES NLX AND NLY IN DATA UNITS. THIS IS A RT11 PROGRAM AND IS COMPATIBLE WITH TDHAND.FOR.

BYTE ESC, I0H
ESC="30. TYPE 1, '+'ESC
FORMAT(2A1, '+dR') ! TURN ON GRAPHICS CURSOR.
TYPE 3
FORMAT('AM THE CURSOR PROPERLY POSITIONED? >')
ACCEPT 2, I0H
FORMAT(A1)
IF(I0H.EQ.'Y') GO TO 4
GO TO 10
TYPE 5, '+'ESC
FORMAT(2A1, '+s3') ! READS CURSOR POSITION.
TYPE 6, '+'ESC
FORMAT(2A1, 'gR') ! RESETS TERMINAL
ACCEPT 7, L0H, L1H ! L0H AND L1H ARE CURSOR COORDINATES IN GRAPHICS UNITS.
FORMAT(16, X, I6)
THE NEXT CODE CONVERTS GRAPHICS UNITS TO DATASET UNITS. AUTOPLOT CORNERS ARE AT (70, 45), (70, 349), (684, 349), (684, 45).

NLX=IFIX((FLOAT(L0H)-70.)*0.5537459)+1
NLY=IFIX(FLOAT(L1H-45)+1.1642)
RETURN
END

TDGCUR.FOR
FUNCTION IGFWAN

THIS SUBROUTINE GETS A FILE NAME FROM THE TERMINAL. IT CHECKS
FOR THE PROPER NUMBER OF CHARACTERS ALSO. THE STRING IS SCANNED
FOR AN EXTENSION. IF ONE DOES NOT EXIST, THEN THE STRING IN
"DEFX" IS APPENDED. A NULL CHARACTER IS PLACED AT THE END OF THE
COMPLETE FILE SPECIFICATION AND THE RESULTANT STRING IS PASSED BACK
TO OTHER SECTIONS VIA A COMMON BLOCK.
+003 THE FUNCTION RETURNS A VALUE DEPENDANT ON WHETHER A CTRL/Z
WAS DETECTED.
| IGFWAN = -1 - CTRL/Z ENTERED AT THE TERMINAL
| IGFWAN = 0 - NO CTRL/Z, NORMAL RETURN, FILE NAME IS VALID |

WRITTEN GREG LIVERMAN 15-JAN-80
++001 MODIFIED GREG LIVERMAN 22-JAN-80
| - ADD END-OF-FILE RETURN CODE |
++002 MODIFIED GREG LIVERMAN 13-FEB-80
| - CHANGED TO LOWER CASE MESSAGES |
++003 MODIFIED GREG LIVERMAN 27-JUN-80
| - CHANGED TO FUNCTION AND CHANGED NAME |
| TO MAKE IT INTEGER BY DEFAULT. EOF |
| CODE IS NOW RETURNED AS FUNCTION RESULT. |

BYTE FILNAM,DEFX(4)
COMMON /FNAME/,FILNAM(16)
DATA DEFX'/',',',',',','/

WRITE OUT THE PROMPT AND READ IN A STRING
WRITE(5,1000)
1000 FORMAT('Filename -- ') READ(5,1001,END=10) NCH,FILNAM
1001 FORMAT(G,16A1)
   IF(NCH.GT.0.AND.NCH.LE.14) GO TO 1
6 WRITE(5,1002)
1002 FORMAT('Filename error. Reenter./')
GO TO 2

SEARCH FOR EXTENSION
DO 3 I=1,NCH
   IF(FILNAM(I).NE.'/') GO TO 3
   IF(I.LT.NCH) GO TO 4
   NCH=NCH-1
   GO TO 5
   CONTINUE
3 CONTINUE

PUT DEFAULT EXTENSION IN
IF(NCH.GT.10) GO TO 6
DO 7 I=NCH+1,NCH+4
   FILNAM(I)=DEFX(I-NCH)
   NCH=NCH+4
7 CONTINUE

PUT IN THE NULL BYTE
FILNAM(NCH+1)=0
GO TO 9
HANDLE EXIT ON EDF FROM TERMINAL
10   IGFNAME=1
     RETURN
     RETURN
RETURN TO CALLING PROGRAM
8     IGFNAME=0
     RETURN
     RETURN
END

TTONOF.MAC

TITLE TTONOFF

THIS FILE CONTAINS TWO SECTIONS WHICH MAY BE USED TO TURN THE
"SPECIAL TERMINAL MODE" BIT IN THE JOB STATUS WORD ON OR OFF. THE
"SPECIAL MODE" ALLOWS A PROGRAM IMMEDIATE ACCESS TO CHARACTERS
TYPED ON THE CONSOLE TERMINAL. SEE THE "ADVANCED PROGRAMMERS GUIDE"
FOR MORE INFORMATION. THE TERMINAL RING BUFFER IS EMDPTED AFTER
TURNING THE BIT ON OR OFF. THESE MAY BE CALLED AS SUBROUTINES
FROM FORTRAN.

NOTE THAT THESE ROUTINES USE THE STACK FOR TEMPORARY STORAGE
(1 WORD). THE STACK POINTER (R6) SHOULD CONTAIN A VALID READ/WRITE
ADDRESS!!

WRITTEN GREG LIVERMAN 23-JAN-80

TTBIT=10000
JSW=4
TTWAIT=100

.MCALL TTRIN
ENTRY POINT FOR TURN ON

TTON:
   BIG   #TTBIT.8@JSW       ;SET SPECIAL MODE BIT
   RDCH:  MOV  @JSW, -(SP)  ;SAVE OLD JSW
   BIS   #TTWAIT, @JSW     ;MAKE SURE WE DON'T WAIT
   TTRIN  BCC  1*          ;SEE IF CHARS AVAILABLE
   MOV  (SP)+, @JSW         ;REPLACE OLD JSW
   RETURN
ENTRY POINT FOR TURN OFF

TTOFF:
   BIG   #TTBIT.8@JSW       ;CLEAR SPECIAL MODE BIT
   BR  RDCH                  ;GO CLEAR THE BUFFER

END
SUBROUTINE FOR WAITING A SPECIFIED PERIOD OF TIME
TO BE CALLED FROM FORTRAN. MAY BE CALLED FROM ASSEMBLER
CONFORMS TO PDP-11 CONVENTION FOR CALLING ASSEMBLY
LANGUAGE SUBROUTINES FROM FORTRAN... SEE FORTRAN REFERENCE
MANUAL FOR DETAILS.
DOES NOT PRESERVE REGISTERS!!!

WRITTEN - GREG LIVERMAN 19-JUN-79

.TITLE WAIT PROGRAM TO WAIT FOR AWHILE
.MCALL..V2..REGDEF..GTIM..EXIT..PRINT
..V2..
..REGDEF
..DEFINE ALL THE REGISTERS
..GLOBAL WAIT
..NAME OF SUBROUTINE
..GLOBAL, OF COURSE

WAIT:
..START HERE
CMP #3,(R3)+
ONE ERR1
MAKE SURE ALL THE
ARGUMENTS ARE THERE
CLR TIM
SET UP REGISTERS AND JUNK
CLR <TIM+2>
MOV #CONST,R2
MOV #3,R3

CONV:
MOV @(R3)+,R0
CONVERT HOURS, MINUTES
AND SECONDS INTO CLOCK
TICKS
CLC
MUL (R2)+,R0
BCS ERR2
ADD R1,<TIM+2>
ADC TIM
ADD R0,TIM
BCS ERR3
SUB R3,CONV

.FTIM #LIST,#TIME
FIND OUT WHAT TIME IT IS NOW
ADD <TIME+2>,<TIM+2>; ADD THAT TO HOW LONG WE WAIT
ADC TIM
ADD TIME,TIM
BCS ERR4

.WTLP:
.FTIM #LIST,#TIME
CHECK THE TIME AGAIN
CMP TIM,TIME
BHI WTLP
SEE IF WE CAN STOP WAITING
CMP <TIM+2>,<TIME+2>
BHI WTLP

RTS PC
GET THE HELL OUT OF DODGE

EXIT

ERR1:
PRINT #EMES1

EXIT

ERR2:
PRINT #FMFR2
ERR3: PRINT #EMES3
ERRY: PRINT #EMES4

; STORAGE AREA

TIME: .WORD 0.0
TIM: .WORD 0.0
LIST: .BLKW 2
CONST: .WORD 3600.60.1TR0: .WORD 0
TR1: .WORD 0
TR2: .WORD 0
TR3: .WORD 0

; MESSAGES NEXT
EMES1: .ASCIZ "WRONG NUMBER OF ARGUMENTS - "WAIT" - FATAL/
EMES2: .ASCIZ "MULT. OVERFLOW #2 - "WAIT" - FATAL/
EMES3: .ASCIZ "ADD. OVERFLOW #3 - "WAIT" - FATAL/
EMES4: .ASCIZ "ADD. OVERFLOW #4 - "WAIT" - FATAL/

.EVEN WAIT: PRINT #EMES2
ERRY: .PRINT #EMES3
ERRY: .PRINT #EMES4

; STORAGE AREA

TIME: .WORD 0.0
TIM: .WORD 0.0
LIST: .BLKW 2
CONST: .WORD 3600.60.1TR0: .
LASPPH. FOR IS A PROGRAM FOR HANDLING THE LE CROY TRANSIENT DIGITIZER WHEN DOING LASER FLASH PHOTOLYSIS. IT AVERAGES THE INTEGER KEEPY DATA THAT COMES FROM THE LE CROY IN GROUPS OF THREE CHANNELS.

THE PROGRAM IS CAPABLE OF DOING PURE FIRST ORDER OR PURE SECOND ORDER DATA ANALYSIS AND PLOTTING THE FITTED CURVE THAT RESULTS IN EITHER CASE.

PROVISIONS HAVE BEEN MADE FOR USING THE 50K OP AMP WITH A LE CROY PRETRIGGER SETTING OF 0. THE LE CROY IS TRIGGERED BASED ON ELECTRONICS PSE DESIGNED AND INSTALLED. THE AMOUNT OF BASELINE YOU SEE DEPENDS ON THE SETTING OF THE 6-12-20 SWITCH ON THE PULSE ENERGY MONITOR & TIMING LOGIC BOX. RECOMMENDED SETTINGS ARE SHOWN TO THE PROGRAM USER WHEN LASPPH IS BEGUN.

THIS PROGRAM IS SET UP TO HANDLE DATA ACQUISITION VIA CHOPPED LIGHT.

THE NEEDED SUBROUTINES FOR THIS PROGRAM LIVE IN THE OBJECT LIBRARY LASLIB.OBJ. THE COMMAND FILE LASLIB.COM WILL CREATE THIS LIBRARY FROM ALL THE COMPONENT OBJECT FILES. IT ALSO SHOWS THE FILE NAMES OF THE SUBROUTINES USED. THE FILENAMES DIFFER FROM THE MODULE NAMES IN MOST CASES. TO SEE A LIST OF THE MODULE NAMES TYPE LIBRARY/LIST LASLIB.

LINKING LASPPH IS SIMPLE. NO OVERLAY IS INVOLVED. FOLLOW THE FOLLOWING COMMAND SEQUENCE:

```
LINK/INCL LASPPH, LASLIB
SHORT <CR> <CR>
```

NOTE. THE DOLLAR SIGN IN $SHORT IS SHIFT 4. IT IS NOT AN ESCAPE CHARACTER.

```
LIBRARY/CREATE/PROMPT
LASLIB  
LACOT, COOL, AVLTSG, AVSHAP, FLP, AVGPLT  
TDGCU: FLCAL, FLCLCR, AVGTEC, AVGSET, CBLOCK  
CSGA, CSSA, CREG, WAITF, AVBGSB, TDGFNA  
TDFFCO, AVSETX, PAGE, JERITD, APAGE, FLSETY  
TGSNAP, TDBOR
```

```
KOMSPC.FOR  T. WOODS AND P.S. ENGEL  AUG. 31, 1981

PROGRAM TO ACQUIRE TRANSIENT SPECTRA, USES SUBROUTINES FOOL,
SUREAD, SUBADJ, PAGE, IDT, WAITF, ABSCA, ITPPLT
DIMENSION XLANA(80), OPDA(80), ABRSOR(80), TQTSTP(80), ISAM(80),
* OPAVE(80), PHOTAV(80), PULAVE(80), PULEN(80), PHOT(80), HVOLT(80),
* NSKIP(8)
COMMON/FINDAB, IDBUF(250), ISAMP, NSK, ILE CDRY DATA
* BYTE FILNAM(16), ANS, SPECID(80), DAIT(9), THYME(8), ESC
COMMON/ACOM/START, STOP, DACA1, LMPFLQ ! FOR SUBADJ
COMMON/TDCOM/ITDNUM, ITDFLQ ! FOR ITD
COMMON/SUBCOM/DACA0, ADADR, GAIN. OR3AD ! FOR SUREAD AND FOOL
INTER@=2 DACA0, DACA1, ADADR, OR3AD, TDADR, CDREG, IPFBUF(2)
DATA ESC/"32/
LOGICAL=1 0, LMPFLQ
DATA ISAM/0, 5000, 5000, 500, 500, 500, 500, 500, 500,
DATA NSKIP/0, 0, 0, 0, 3, 6, 10, 23/
!RISE TIME AND LASER LIGHT SKIP CH
ITDNUM=16
CALL ITDSET
DACA0=CDREG(1, 5, 12, 0) ! DA/12 CH. 0 FOR NULLING
DACA1=CDREG(1, 5, 12, 1) ! DA/12 CH. 1 FOR PMT HV
ADADR=CDREG(1, 5, 13, 0) ! BI-RA ADDRESS, AE=0
OR3AD=CDREG(1, 5, 15, 0) ! OR3-ADDRESS
TDADR=CDREG(1, 5, 16, 0) ! LECDRO TO ADDRESS
9000 TYPE 9001, "1", ESC
9001 FORMAT(2A1, "1") ! NEXT ALPHANUMERIC PAGE. DON'T CLEAR
CALL PAGE ! CLEAR SCREEN OF ANY GRAPHS.
TYPE 850
850 FORMAT('LOOK AT THE 6-12-20 SWITCH ON THE TIMING LOGIC AND /
* PULSE ENERGY MONITOR BOX. CERTAIN SETTINGS ARE RECOMMENDED /
* IN ORDER TO FILL ENOUGH CHANNELS WITH BASELINE INFORMATION /
* YET NOT WASTE CHANNELS WITH TOO MUCH BASELINE. THE DELAY /
* SETTING IS RELATED TO THE NSSEC/CHANNEL LE CROY SETTING IN /
* THE FOLLOWING WAY /
* NSSEC/CHANNEL MICROSECOND TIME DELAY SETTING /
* 50 5 /
* 100 12 /
* 200 12 /
* 500 20 /
* 1000 20 /
TYPE 5
5 FORMAT('ENTER A 1 IF YOU ARE USING XENON LAMP /
* ENTER A 0 FOR TUNGSTEN LAMP .')
ACCEPt 6, LMPFLQ
6 FORMAT(1I1)
TYPE 1
1 FORMAT('SET MONOCHROMATOR AT DESIRED LONG LIMIT STARTING /
* WAVELENGTH THEN ENTER THAT VALUE IN NM> $)
READ(5, *) LAMLON
START=FLOAT(LAMLON)
TYPE 2
2 FORMAT('ENTER DESIRED SHORT WAVELENGTH LIMIT> $)
READ(3, *) LAMHIO
STOP=FLOAT(LAMHIO)
TYPE 3
3 FORMAT('ENTER DESIRED NUMBER OF NM BETWEEN POINTS. /
* USE 5, 10, OR 20 NM > $)
READ(5, *) INT
TYPE 559
559 FORMAT('ENTER THE AMPLIFIER GAIN ')
ACCEPt *, GAIN
TYPE 4
4 FORMAT('ENTER THE DESIRED NUMBER OF LASER SHOTS PER WAVELENGTH /
* SETTING> $')
HEAD: \$ + NSHOT
CALL CSSA(27, TDAGR, 1) ! DIGITIZE OFFSET
CALL CSSA(1, TDAGR, IFPDAT, 1)
IF NOT G1 GO TO 57
IOFF = (IFPDAT AND "177700") / 64 ! CALCULATE FRONT PANEL OFFSET
1 TYPE 6, IFPDAT
FORMATE: (IFPDAT = '07')
2 TYPE 9, IFF
3 FOMAT: ('IOFF = '15')
ISAMP = ISAM(IFPDAT AND "7") ! FIND NSC/CHANNEL
NSK = NSK (IFPDAT AND "7") ! RISE TIME AND SCATTERED LASER SKIP
NSK = NSK + 2
4 TYPE 4, NSK
CALL CSSA(2b, ADAIR, 1)
CALL CSSA(1b, DACAO, 2048, 1)
NPTS = 1 + (LAMON - LAMSHO) / INT;
TOTSTEP = 1 / INT = 0
5 STEPS = 40
NPARRA = NPTS * INT / 5
DO 10 N = 1, NPARRA
6 LAMDA(N) = FLOAT(LAMON - (N - 1) * INT) ! WAVELENGTH ARRAY FOR PLOT
DESLAM = FLOAT(LAMON - (N - 1) * 5)
ACTLAM = FLOAT(LAMON) - TOTSTEP * INT = 1.313
ERROR = DESLAM - ACTLAM ! DESIRED - ACTUAL WAVELENGTH
7 IF (ERROR GE 0.) GOTO 40
8 TAKES ONE LESS STEP IF ERROR ACCUMULATES TOO MUCH
9 STEPS = 40
10 GO TO 60
10 STEPS = 310
10 TOTSTEP(N + 1) = TOTSTEP(N) + STEPS
INDEX = INT / 5
9 TYPE 600
110 FORMAT: (AFTER SHUTTER OPENS, ADJUST SLIT FOR DESIRED PMT OUTPUT) ! = CONTROL I CONTINUES. ENTER A 1 WHEN READY TO START. 
5 ACCEPT 8.10
CALL CSSA(16, ORJAD, '42.0') ! OPEN SHUTTER, TURN ON STEP PWR
CALL WAIT(0.0, 10) ! ALLOW TIME TO SETTLE
CALL SUBADJ(2.0, START, VOLT) ! INITIAL HV SETTING
500 TYPE 602, VOLT
502 FORMAT: ('INITIAL HV = ', FB, 2)
50 DO 101 I = 1, 1100
50 CALL SUREAD(1.0, 1.0, PMT)
51 TYPE 602, PMT
52 FORMAT: ('PMT OUT = ', FB, 3)
53 IF (ITITN = I.EQ. '32') GO TO 603
601 CALL WAIT(0.0, 20)
603 PHOLAS = PMT
CALL POOL(0.1)
CALL CSSA(16, ORJAD, '62.0') ! NULLS OFFSET FIRST
CALL WAIT(0.0, 20) ! OP AMP RELAY ON
CALL SUBADJ(2.0, PHOLAS, PMT, WAIT, VOLT)
VOLT(J) = VOLT
CALL POOL(1.1)
2 THE NEXT ROUTINE FIRE THE LASER NSHOT TIMES
3 CHANGE FROM 150 TO 250 ON 1-7-82
DO 101 I = 1, NSHOT
10 CALL IDIBUF, IPBUF, NSHOT, 350)
2 START LECROY PD
DO 10 J = 1, NSHOT
CALL SUREAD(0.1, 1.1, OUT)
10 OPUT(J) = OUT
OPUT(J) = OPUT(J) + OPTOT
OPTOT = OPUT(J)
CALL SUREAD(1.1, 1.1, PMT)
PHOT(J) = PMT
PHOT(J) = PHOT(J) + PHOT(J)
CALL CSSA(16, ADADR, 2, 0) \ SETS BI-RA TO READ PULSE ENERGY
CALL CSSA(16, OR3AD, "72, G) \ INTEGRATOR RESET PULSE TO CH. 4
CALL CSSA(21, OR3AD, "10, Q) \ END RESET PULSE
CALL CSSA(16, OR3AD, "43, G) \ FIRE LASER (CH. 1)
CALL CSSA(21, OR3AD, "1, Q) \ END LASER PULSE

113 CALL CSSA(0, ADADR, IPULS, G) \ READ OUT PULSE ENERGY (CH. 2)
IF( NOT G) GO TO 113
IPULS=4095-IPULS \ CONVERTS NEG. IPULS TO POS.

30 PULLEN(J)=FLOAT(IPULS))/400.0 \ CONVERTS ANSWER TO VOLTS
10 PULTOT=PULTOT+FULEN(J)

J=PHOTAV(J)=PHOTAV/FLOAT(NSHOT) \ AVERAGE OP AMP OUTPUT
PULAVE(J)=PULTOT/FLOAT(NSHOT) \ AVERAGE PMT OUTPUT
CALL ABECA(J, GAIN, ABSB, PHOTAV(J), NSHT) \ CALCULATE THE ABSORBANCE.

NB=ABSBN(J)=ABSBN
NPTSN=IFIX((TSTP((INDEX+J)+1)) - TSTP((INDEX+(J-1)+1)))
DO 17 J=1, NPTSN
CALL CSSA(16, OR3AD, "462, G) \ START STEPPER PULSE
CALL WAIT(0, 0.3)
17 CALL CSSA(21, OR3AD, "440, G) \ STOP STEPPER PULSE
GO TO 101

50 TYPE 52
52 FORMAT(//, 'ENTER 1 TO CONTINUE SCAN. 0 TO SKIP THE REST.: ', I)
READ(5, *) J
IF(J.EQ. 0) GO TO 53

101 CONTINUE
53 CALL WAIT(0, 0.3)
CALL CSSA(9, OR3AD, D, G) \ CLOSE SHUTTER, RESET OR-3
CALL CSSA(24, ADADR, D, 0) \ HIBIBIT BI-RA'S RUN MODE
NPTSN=J-1 \ ALLOWS FOR EARLY EXIT FROM WAVE. SCAN

C NEXT ROUTINE NORMALIZES ABSORBANCE FOR VARYING PULSE ENERGY

TPTUL=90.0
DO 81 J=1, NPTSN
PULAVE(J)=PULAVE(J)+PULAV(J)
TPTUL=TPTUL+PULAVE(J) \ TOTAL PULSE ENERGY AT ALL LAMBDAS
AVEPUL=TPTUL/FLOAT(NPTSN) \ AVERAGE OF ALL PULSE ENERGIES
DO 32 I=1, NPTSN
FACNOR=AVEPUL/PULAVE(J) \ NORMALIZATION FACTOR
32 ABSRB(I)=ABSBS(I)+FACNOR
GO TO 35

30 TYPE 34, 1
34 FORMAT(//, 'PULSE ENERGY NO., ', I3, ' WAS LESS THAN 0.01 VOLTS.', / 
\ ' PULSE ENERGY NORMALIZATION ROUTINE WAS BYPASSED. ')

35 TYPE 82
35 FORMAT('DO YOU WANT A TYPED LIST OF LAMBD.A AND ABSORBANCE?')
ACCEPT 91, ANS
IF(ANS.NE. 'Y') GO TO 84

77 TYPE 77
77 FORMAT('C' / 'C WAVE. ', 2X, 'ABSBR. ', 2X, 'OPUT. ', 1X, 'OPAVE. ', 2X, 
\ \ 'PHOT. ', 2X, 'PHOTAV. ', 2X, 'PUL', 2X, 'PULAVE. ', 2X, 'H/V' / 'C')
DO 83 I=1, NPTSN
WRITE(5, 85) XALMDA(I), ABSBR(I), OPUT(I), OPVE(I), PHOT(I), 
\ \ PHOTAV(I), PUL(I), PULAVE(I), HVOLT(I)
83 CONTINUE
WRITE(5, 97) GAIN, NSHOT, IFDPAT, ISAMP
97 CONTINUE
WRITE(5, 97) GAIN=, 'F4. 1', NSHT=' ', I3, IFDPAT=' ', 0.7, 
\ \ NSEG=' ', I4

84 TYPE 84
84 FORMAT('DO YOU WANT A PLOTTED ABSORBANCE SPECTRUM?')
ACCEPT 91, ANS
IF(ANS.NE. 'Y') GO TO 87
CALL STPLT(1, XALMDA, ABSBR, NPTSN)
TYPE 86
FORMAT('"DO YOU WANT TO PUT THE SPECTRUM IN A FILE?"')
ACCEPT 91, ANS
IF(ANS NE 'Y') GO TO 96
CALL DATE(DAIT)
CALL TIME(THME)
TYPE 89
FORMAT('"OUTPUT FILENAME?"')
ACCEPT 91, (FILNAM(I), I=1, 15)
FORMAT(' *GOA*')
FILNAM(1G*0)
OPEN(UNIT=2, NAME=FILNAM, TYPE='NEW')
WRITE(2, 92)(DAIT(I), I=1, 9)
WRITE(2, 92)(THME(I), I=1, 8)
WRITE(2, 92)(FILNAM(I), I=1, 15)
TYPE 90
FORMAT(' *ENTER A SPECTRUM ID. YOU HAVE 77 CHARACTERS.*')
ACCEPT 91, (SPECID(I), I=1, 77)
WRITE(2, 92)(SPECID(I), I=1, 77)
FORMAT(' C ', 79A1)
WRITE(2, 7007) NPTS
7007 FORMAT(' C ', 16 'WAVELENGTH POINTS')
WRITE(2, 77)
DO 93 I=1, NPTS
WRITE(2, 85)(X(LAMDA(I), ABSORB(I), DOPUT(I), OPAVE(I), PHOT(I),
PHOTAV(I), PULLEN(I), PULAVE(I), HVOLT(I)
93 CONTINUE
IF(LMPFLG.EQ.0) WRITE(2, 400)
FORMAT(' C TUNGSTEN LAMP')
IF(LMPFLG.EQ.1) WRITE(2, 401)
FORMAT(' C XENON LAMP')
WRITE(2, 97) GAIN, NSHOT, IFTPAT, ISAMP
CLOSE(UNIT=2)
95 TYPE 96
FORMAT(' *DO YOU WANT TO OBTAIN ANOTHER SPECTRUM?*')
ACCEPT 91, ANS
C
NOW RETURN STEPPER TO ORIGINAL POSITION
CALL CSSA(15, ORJAD, "40.0") 'TURN ON STEPPER POWER AGAIN
KKK=TSTOP(NPARA)
DO 65 I=1, KKK
CALL CSSA(15, ORJAD, "240.0")
CALL CSSA(21, ORJAD, "200.0")
CALL WAIT(0.0, 1)
CALL CSSA(9, ORJAD, D, G) 'TURN OFF STEPPER POWER
IF(ANS.EQ."Y") GO TO 9000
STOP
END
SUBROUTINE ABSCAL(GAIN, ABSS, PHOTAV, NSHOT)
COMMON/FINDAB/IDBUF(350), ISAMP, NSK
! LE CROV DATA

C THIS SUBROUTINE FINDS THE MAXIMUM ABSORPTION AT A GIVEN WAVELENGTH.
C 2-FEB-81 T. WOODS
C
NCHIO=2000/ISAMP ! NO. CHANNELS IGNORED, OP AMP NOT ON YET.
C FIND THE MAXIMUM INTENSITY OF THE DECAY CURVE = MINIMUM IDBUF VALUE.
C TEMP=32767 ! ARBITRARILY LARGE INITIAL VALUE.
SUM=0
IXMAX=0 ! THE CH. NO. CORRESPONDING TO THE MINIMUM IDBUF VALUE
DO 60 I=NCHIO+1, 390
IF((IDBUF(I)+1)-IDBUF(I), GE, 3+IFIX(SQRT(FLOAT(NSHOT)))) GO TO 60
C THE ABOVE IS A TEST TO SEE IF WE'RE ON WELL BEHAVED PART OF THE DECAY
C CURVE.
LITEMP=MINE(IDBUF(I), LITEMP)
IF(LITEMP EQ. IDBUF(I)) IXMAX=I
60 CONTINUE
XMIN=FLOAT(LITEMP) ! MAX INTENSITY=MIN IDBUF VALUE IS FOUND.
C NOW FIND THE BASELINE.
DO 70 I=NCHIO+1, IXMAX-NSK
70 SUM=(SUM+IDBUF(I))
XSUM=XSUM
BSLE=XSUM/FLOAT(IXMAX-NCHIO-NSK) ! BASELINE FOUND
AVEV1=PHOTAV*1000. ! LIGHT ON PMT OUTPUT IN MILLIVOLTS.
VOSCF=2./(GAIN*FLOAT(NSHOT)) ! VOLTAGE SCALING FACTOR FOR LE CROV DATA
DIF=BSLE-XMIN
ABSS=ABS((AVEV1/(AVEV1-((DIF)*VOSCF)))) ! ABSORPTION FOUND
RETURN

FOOL.FOR

SUBROUTINE FOOL (RLYFLG, STPFLG) ! P.S. ENGEL 8/20/81
C NUTS PNT OUTPUT USING CHOPPED LIGHT AND SUBROUTINE SUREAD
COMMNCH/SUBCH/DAACO, ADDR, GAIN, OR3AD
INTEGER*2 DAACO, ADDR, G3AD
LOGICAL*1 G, RLYFLG, STPFLG
C NEXT ROUTINE READS PHT AND OP AMP OUTPUT ON SUCCESSIVE CHOPPER
C LIGHT PULSES.
CALL SUREAD(1, RLYFLG, STPFLG, PHOTA) ! READ PNT
CALL SUREAD(0, RLYFLG, STPFLG, OPOUTA) ! READ OP AMP OUTPUT
TYPE 200, OPOUTA, PHOTA
200 FORMAT(/' OP=",F7.3,' PMT=',F7.3) ! TYPES VALUES BEFORE NULLING
J=0
501 IADJ=IFIX((PHOTA*400.0+1995.)*1.024) ! MAKES OFFSET V = PNT V
J=J+1
502 CALL CSSA(16, DAACO, IADJ, G) ! WRITES OFFSET VOLTAGE TO DA/12
CALL SUREAD(1, RLYFLG, STPFLG, PHOTA) ! READ PNT
CALL SUREAD(0, RLYFLG, STPFLG, OPOUTA) ! READ OP AMP OUTPUT
7 TYPE 400, OPOUTA, PHOTA
400 FORMAT(/IX,2F7.3)
IF(J, GE, 6) GO TO 10 ! ONLY GETS 6 TRIES TO NULL
IF(OPOUTA, LE, -.1) GO TO 501
IF(OPOUTA, GE, .01) GO TO 501
IF(OPOUTA, LE, .02) GO TO 501
CORR=(OPOUTA/GAIN)*409.6 ! CORRECTS IADJ IF WE'RE CLOSE
IADJ=IADJ+IFIX(CORR)
GO TO 502
10 RETURN
END
SUBROUTINE STPPLT(X,Y,N)
DIMENSION X(N),Y(N)
BYTE ESC
DATA ESC/*33*/
TYPE 29.0,ESC
FORMAT(2A1, 'U')
TYPE 38.0,ESC
FORMAT(2A1, 'S')
CALL PAGE
TYPE 5, ' + ', ESC
FORMAT(2A1, '*dA')
SMABS=0.
CALL BIGNO(Y,N,BIGABS)
BIGABS=BIGABS+1.
DELTA=(BIGABS-SMABS)/10.
TYPE 1, ' + ', ESC, X(N), X(1), SMABS, BIGABS, DELTA, DELTA, N
FORMAT(2A1, ' + Z' )
TYPE 6, ' + ', ESC
FORMAT(2A1, ' + a 0v 0w c z' )
CALL WAIT(0.3, 0)
TYPE 2, ' + ', ESC
FORMAT(2A1, ' + aZ' )
DO 3 I=1,N
WRITE(5,4) X(I),Y(I)
4 FORMAT(F14.7, X, E15.6)
IF(ITTNR().EQ. '32') GO TO 100
TYPE 7, ' + ', ESC
FORMAT(2A1, ' K' )
TYPE 8, ' + ', ESC
FORMAT(2A1, ' A' )
CONTINUE
100 TYPE 29.0, ESC
TYPE 38.0, ESC
RETURN
END

STPPLT.FOR plots the absorption spectrum of the transient on the HP2648A graphics terminal.
SUBROUTINE SUBADJ(PHOLAS, WAVE, HVOLT) ! P.S. ENGEL B/19/81
WRITES PROPER CONTROL VOLTAGE TO PMT POWER SUPPLY
COMMON/ADCGM/START, STOP, DCA1, LMPFLG
INTEGER*2 DCA1
LOGICAL*1 LMPFLG ! LMPFLG=1 MEANS XENON LAMP
SIGNAL(WAVE)=100. *(291.1-321.6*(WAVE/100.))+125.2*
* WAVE/100. )**3-2.20.04*(WAVE/100. )**3+1.129*(WAVE/100. )**4*
SIGNAL(WAVE)=100. *(1342. 0-1196. 4*(WAVE/100. ))+384. 56*
* WAVE/100. )**2-52. 488*(WAVE/100. )**3+2. 579*(WAVE/100. )**4*
IF(LMPFLG, EQ. 1.) GO TO 2
SIGMIN=SIGNAL(START)
IF(SIGMIN, GT, SIGNAL(STOP)) SIGMIN=SIGNAL(STOP)
HVOLT=130. *(PHOLAS*SIGMIN/SIGNAL(WAVE)+5.3)
GO TO 3
2 SIGMIN=SIGNAL(START)
IF(SIGMIN, GT, SIGNAL(STOP)) SIGMIN=SIGNAL(STOP)
HVOLT=130. *(PHOLAS*SIGMIN/SIGNAL(WAVE)+5.3)
3 IVOLUME=IFIX(2048. 0-2. 228*HVOLT)
IF(WAVE, GT, 920. 0) IVOLUME=0
IF(HVOLT, GT, 920. 0) TYPE 5, WAVE
4 FORMAT(‘WAVE=’,F7. 2,2X,‘HV=’,F7. 2)
5 FORMAT(‘HVOLT WAS GREATER THAN 920V AT ’,F7. 1,‘NM’)!
CALL CSSA(16, DCA1, IVOLUME) ! WRITES VOLTAGE TO DA/12
RETURN
END

SUBROUTINE SUREAD(ICHAN, RLVFLO, STPFLG, PHOT) ! P.S. ENGEL B/20/81
READS BI-RA VOLTAGE USING CHOPPED LIGHT. ICHAN IS 0 FOR OR AMP.
1 FOR PMT OUTPUT. RELAY CLOSED IF RLVFLO=1. STEPPER PWR ON IF
STPFLG=1.
COMMON/SUBCM/DACAO, ADADR, GAIN, OR3AD
INTEGER*2 DACAO, ADADR, OR3AD
LOGICAL*1 RLYFLO, STPFLG
IDAT=’102
IF(RLYFLO, EQ. 1. AND. STPFLG, EQ. 0.) IDAT=’122
IF(RLYFLO, EQ. 1. AND. STPFLG, EQ. 1.) IDAT=’162
:STPFLG, EQ. 0. AND. STPFLG, EQ. 1.) IDAT=’142
RETURN
CALL CSSA(16, ADADR, ICHAN, Q) ! SET BI-RA TO DESIRED CHANNEL
CALL CSSA(16, OR3AD, IDAT, Q) ! SET FLIP FLOT
CALL CSSA(21, OR3AD, ’100. 0) ! RESET FLIP FLOT
CALL CSSA(0, ADADR, IPHOT, Q) ! TRY TO READ PHT
IF(.NOT. Q) GO TO 1
:CYCLE UNTIL CHOPPER ALIGNED
IF(IPHOT, LE, 2047) GO TO 2
:FOR NEGATIVE VOLTAGES
PHOT=(FL0AT(IPHOT))/400. 0
RETURN
END
ABSORPTION SPECTRA FOR TRANSIENTS GENERATED BY PULSED LASER FLASH PHOTOLYSIS CAN BE OBTAINED BY USING THE PROGRAM 'KOMSPC.FOR'.

*KOMSPC IS LINKED AS FOLLOWS.
  LINK/INCL KOMSPC, SPOLIB, CMCLIB
  *SHORT <CR> <CR>
THE DOLLAR SIGN IS SHIFT 4 NOT AN ESCAPE CHARACTER. <CR> IS THE SYMBOL FOR CARRIAGE RETURN.
SPOLIB IS AN OBJECT LIBRARY THAT CONTAINS ALL THE OBJECT FILES FOR THE SUBROUTINES REQUIRED BY KOMSPC. THE CAMAC SUBROUTINES ARE NOT INCLUDED IN SPOLIB. THE CAMAC SUBROUTINE OBJECT FILES LIVE IN CMCLIB.

A SEPARATE PROGRAM EXISTS CALLED SEPPLT.FOR THAT WILL READ A KOMSPC GENERATED DATA FILE AND PLOT THE RESULTING ABSORPTION SPECTRUM. THIS VERSION OF SEPPLT WAS CREATED 8-SEP-81 AND IS COMPATIBLE WITH KOMSPC DATA FILE FORMAT WHICH IS DIFFERENT FROM PREVIOUS SPECTRA PROGRAMS LIKE JOMSPC'S DATA FILE FORMAT. SEPPLT IS LINKED AS FOLLOWS.
  LINK SEPPLT, WAITF, SIGNO, PAGE
SUBROUTINE SIGND(X, N, SIG)
DIMENSION X(N)
C THIS SUBROUTINE FINDS THE MAXIMUM VALUE OF A REAL ARRAY OF SIZE, N.
   TEMPI=1.E5
   DO 10 I=1,N
      TEMP=AMAX1(TEMP, X(I))
   10 SIG=TEMP
   RETURN
END
KOMSPC.FOR (special)

PROGRAM TO ACQUIRE TRANSIENT SPECTRA, USES SUBROUTINES FOOL,
SUREAD, SUBADJ, PAGE, ITD, WAITF, Aalborg, STPPLT
THIS MODIFIED PROGRAM ALLOWS YOU TO KEEP CRUDE DECAY CURVE DATA.
DIMENSION XLANDA(80), SPOUT(80), absor(80), TOTSTOP(80), ISAM(80).
* DAVE(80), PHOTAV(80), PULAVE(80), PULLEN(80), PHOT(80), HVOLT(80).
* NSKIP(8)
DIMENSION IPSAV(390, 16), Bases(16), DECMAX(16), BSX(16), DCX(16)
DIMENSION ABNOT(80)
COMMOM/FINDAB/IDBUF(390), ISAMP, NSK      ! LE CROY DATA
BYTE FLENAM(16), ANS, SPECID(80), DAIT(9), THYME(8), ESC
COMMOM/ADCOM/START, STOP, DACA1, LMPFLG ! FOR SUBADJ
COMMOM/TDCOM/ITDNUM, ITDFLG ! FOR ITD
COMMOM/SUBCOM/DACA0, ADDR, GAIN, CR3AD ! FOR SUBREAD AND FOOL
COMMOM/EXT/XMIN, BSLE, BASEX, DECY
INTEGER#2 DACA0, DACA1, ADDR, CR3AD, TDADR, CREG, IPSBUF(2)
DATA ESC/*33/
LOGICAL#1 G, LMPFON
DATA ISAM/0, 0000, 1000, 5000, 200, 100, 50/ ! POSSIBLE NSSEC/CH
DATA NSKIP/0, 0, 0, 2, 3, 6, 10, 23/ ! RISE TIME AND LASER LIGHT SKIP CH
ITDNUM=16
CALL ITDSET
DACA0=CDREG(1, 3, 12, 0)  ! DA12 CH. 0 FOR NULLING
DACA1=CDREG(1, 5, 12, 1)  ! DA12 CH. 1 FOR PMT HV
ADADR=CDREG(1, 5, 13, 0)  ! BI-RA ADDRESS, A=0
OR3AD=CDREG(1, 5, 15, 0)  ! OR-3 ADDRESS
TDADR=CDREG(1, 5, 16, 0)  ! LECROY TD ADDRESS

9000 TYPE 9001, ' + ', ESC
9001 FORMAT(2AI, 'U')      ! NEXT ALPHANUMERIC PAGE. DON'T CLEAR.
   CALL PAGE      ! CLEAR SCREEN OF ANY GRAPHS.
   TYPE 850
850 FORMAT(' LOOK AT THE 6-12-20 SWITCH ON THE TIMING LOGIC AND ')
   FORMAT(' PULSE ENERGY MONITOR BOX. CERTAIN SETTINGS ARE RECOMMENDED ')
   FORMAT(' IN ORDER TO FILL ENOUGH CHANNELS WITH BASELINE INFORMATION ')
   FORMAT(' YET NOT WASTE CHANNELS WITH TOO MUCH BASELINE. THE DELAY ')
   FORMAT(' SETTING IS RELATED TO THE NSSEC/CHANNEL LE CROY SETTING IN ')
   FORMAT(' THE FOLLOWING WAY: ')
   FORMAT(' NSSEC/CHANNEL MICROSECOND TIME DELAY SETTING ')
   FORMAT(6X, 3A6)  ! 6/ ' 50 6/ ' 100 12/ ' 200 12/ ' 500 20/ ' 1000 20/ ')

TYPE 5
5 FORMAT(' ENTER A 1 IF YOU ARE USING XENON LAMP ')
   FORMAT(' ENTER A 0 FOR TUNGSTEN LAMP. ')
   ACCEPT 8, LMPFON
8 FORMAT(1)
TYPE 1
1 FORMAT(' SET MONOCHROMATOR AT DESIRED LONG LIMIT STARTING ')
   FORMAT(' WAVELENGTH THEN ENTER THAT VALUE IN NM:*$
REAd(5, *) LAMLON
START=FLOAT(LAMLON)
TYPE 2
2 FORMAT(' ENTER DESIRED SHORT WAVELENGTH LIMIT:$
REAd(5, *) LAMSHD
STOP=FLOAT(LAMSHD)
TYPE 3
3 FORMAT(' ENTER DESIRED NUMBER OF NM BETWEEN POINTS. ')
   FORMAT(' USE 5, 10, OR 20 NM : ')
   READ(5, *) INT
   ACCEPT ' , GAIN
TYPE 4
599 FORMAT(' ENTER THE AMPLIFIER GAIN: ')
   ACCEPT ' , GAIN
   TYPE 999
FORMAT(//' ENTER THE DESIRED NUMBER OF LASER SHOTS PER WAVELENGTH
                  SETTING'S)
READ(5,=NSHOT
      CALL CSSA(27, TDADR, , G) ! DIGITIZE OFFSET
      CALL CSSA(1, TDADR, IFPDAT, G) ! READ OUT FRONT PANEL DATA
      IF( NOT(0)) GO TO 57
      IOFF=(IFPDAT AND "177700")/64 ! CALCULATE FRONT PANEL OFFSET
      TYPE 6, IFPDAT
      FORMAT(//' IFPDAT='', 07)
      TYPE 9, IOFF
      FORMAT(//' IFPDAT='', 15/)
      ISAMP=ISAMP((IFPDAT AND "7")+1) ! FIND NSAMP/CHANNEL
      NSK=NSK(IFPDAT AND "7")+1 ! RISE TIME AND SCATTERED LASER SKIP
      NSK=NSK+9 ! MORE SKIPPED CHANNELS NEEDED.
      TYPE 6, NSK
      CALL CSSA(26, ADADR, , G) ! SET BI-RA TO RUN MODE
      CALL CSSA(18, DACK, 2048, G) ! SET DAC TO ZERO OUTPUT
      NPTS=1+(LAMDA0-LAMBA0)/INT ! CALCULATE NO. OF WAVELENGTHS
      TOTSTP(1)=5.0 ! SET UP THE TOTAL STEPS ARRAY
      STEPS=4/0
      NPARR=NPTS/INT/5
      DO 60 M=1, NPARR
      LAMDA(M)=LAMDA0+(M-1)*INT ! WAVELENGTH ARRAY FOR PLOT
      DESLAM=FLOAT(LAMDA0-((N-1)+3))
      ACTLAM=FLOAT(LAMDA0)-TOTSTP(N)*1.313
      ERROR=DESLAM-ACTLAM ! DESIRED - ACTUAL WAVELENGTH
      IF(ABS(ERROR GE 0.9)) GO TO 40
      TAKES ONE LESS STEP IF ERROR ACCUMULATES TOO MUCH
      STEPS=4/0
      GO TO 60
      STEPS=3
      60 TOTSTP(N+1)=TOTSTP(N)+STEPS
      INDEX=INT/5
      TYPE 600
      600 FORMAT(//' AFTER SHUTTER OPENS, ADJUST SLITS FOR DESIRED PMT OUTPUT'//
                  ' CONTINUE Z CONTINUES. ENTER A 1 WHEN READY TO START. '
                  ' ACCEPT B, 10
      CALL CSSA(18, OR3AD, "42.0") ! OPEN SHUTTER, TURN ON STEP PWR
      CALL WAIT(0.0, 10) ! ALLOW TIME TO SETTLE
      CALL SUBADJ(2.0, START, VOLT) ! INITIAL HV SETTING
      TYPE 802, VOLT
      802 FORMAT(//' INITIAL HV= ', FB.2)
      DO 601 I=1, 100
      CALL SUREAD(1.0, 1, PMT)
      TYPE 802, PMT
      602 FORMAT(//' PMT OUT=', FB.3)
      IF( I FF568(1, , 32) ) GO TO 603
      DO 1001 J=1, NPTS
      OPTOT=0.0
      PHOLAS=PMT
      CALL FOOL(0.1) ! NULLS OFFSET FIRST
      CALL CSSA(18, OR3AD, "62.0") ! OP AMP RELAY ON
      CALL WAIT(0.0, 5) ! WAIT FOR RELAY TO CLOSE
      DO 101 J=1, NPTS
      OPTOT=0.0
      PHOTOT=0.0
      WAVE=START-TOTSTP((INDEX(J-1)+1)-1)*1.313
      CALL SUBADJ(2.0, PHOLAS, PMT, WAVE, VOLT)
      HVOLT(J)=VOLT
      CALL FOOL(1.1) ! NULLS THE OFFSET AUTOMATICALLY
      1001 CONTINUE
      DO 10 J=1, NSHOT ! START LECROY TD
      CALL SUREAD(0.1, 1, OUT) ! READ OP AMP
UHUU1(J)=UUU
OPTOT=OPTOT+OPUT(J)
CALL SUREAD(1:1,1,PMT)
PHOT(J)=PMT
PHOT=PHOT+PHOT(J)
CALL CSSA(16,ADADR,2,G)
CALL CSSA(16,ORDAD,72,G)
CALL CSSA(21,ORDAD,10,G)
CALL CSSA(16,ORDAD,63,G)
CALL CSSA(21,ORDAD,11,G)
CALL CSSA(0,ADADR,IPULS,G)
IF( NOT.G) GO TO 113
IPULS=IPULS+IPULS
PUL=IF( NOT.G) GO TO 113
PUL=IPULS/1000.0
OPAVE(J)=OPTOT/FLOAT(NHOT)
PHOTAV(J)=PHOT/FLOAT(NHOT)
PULAV(J)=PUL/FLOAT(NHOT)
CALL ABSCAL(GAIN,ABSO,PHOTAV(J),NHOT)
CALL ABSB(J)=ABSB
NPULS=IPULS*(INDEX*J+1)-TOTALP((INDEX*(J-1)+1))
DO 17 INDEX=1,350
17 CALL CSSA(16,ORDAD,462,G)
CALL WAIT(0.0,3)
CALL CSSA(21,ORDAD,400,G)
STOP STEPPING PULSE
DO 900 INDEX=1,350
BASE(J)=BASE
IF( FITTIN(J), INDEX=32) GO TO 50
100 TYPE 52
52 FORMAT(// ENTER I TO CONTINUE SCAN, 0 TO SKIP THE REST. > *)
READ(0,*) J1
IF(JJ EQ 0) GO TO 50
101 CONTINUE
53 CALL WAIT(0.0,3)
CALL CSSA(9,ORDAD,0,G)
CALL CSSA(24,ADADR,D,G)
NPULS=J+1
NEXT ROUTINE NORMALIZES ABSORBANCE FOR VARYING PULSE ENERGY
TOTPUL=0
81 IF(PULAV(J), LE, 0.01) GO TO 33
81 TOTPUL=TOTPUL+PULAV(J)
AVEPUL=TOTPUL/FLOAT(NPULS)
DO 32 INDEX=1,350
32 ABSB(J)=ABSB(J)*FACOR
GO TO 35
33 TYPE 34, I
34 FORMAT( ' PULSE ENERGY NO. ' , I3 , ' WAS LESS THAN 0.01 VOLTS. '/
PULSE ENERGY NORMALIZATION ROUTINE WAS BYPASED. ')
35 TYPE 82
82 FORMAT( ' DO YOU WANT A TYPED LIST OF LAMBDA AND ABSORBANCE? ')
ACCEPT 9: ANS
IF(ANS, NE, ' Y') GO TO 84
TYPE 77
DO 93 I=1,NPULS
WRITE(3,85) XLAMDA(I), ABSB(I), OPUL(I), PHOT(I), PHOTAV(I), PULAV(I), HVOLT(I)
93 WRITE(3,85) XLAMDA(I), ABSB(I), OPUL(I), PHOT(I), PHOTAV(I), PULAV(I), HVOLT(I)
85 FORMAT(1X,F5.1,1X,F6.3,1X,F7.2)
CONTINUE
WRITE(5,97) GAIN, NSHOT, IFPDAT, ISAMP
97 FORMAT('C'/'C GAIN=',F4.1,' NSHOT=',I3,' IFPDAT=',I3,'07,' + ' NSEC/CH=',I4)
98 TYPE 86
99 FORMAT('DO YOU WANT A PLOTTED ABSORPTION SPECTRUM?\n')
ACCEPT 91,ANS
IF(ANS.NE.\'Y\')GO TO 97
CALL STPPLT(KXLMND,ABSORB,NPTS)
87 TYPE 86
88 FORMAT('DO YOU WANT TO PUT THE SPECTRUM IN A FILE?\n')
ACCEPT 91,ANS
IF(ANS.NE.\'Y\')GO TO 95
CALL DATE(DAHT)
CALL TIME(THMHT)
TYPE 89
90 FORMAT('\n')
ACCEPT 91,(FILNM(I),I=1,15)
91 FORMAT(60A1)
FILNM(16)=0.
OPEN(UNIT=2,NAME=FILNM,TYPE=\'NEW\')
WRITE(2,92)(DAHT(I),I=1,9)
WRITE(2,92)(THMHT(I),I=1,8)
WRITE(2,92)(FILNM(I),I=1,15)
TYPE 90
92 FORMAT('\n\n')
ACCEPT 91,(SPECID(I),I=1,77)
WRITE(2,92)(SPECID(I),I=1,77)
7007 FORMAT('C','16' WAVELENGTH POINTS')
WRITE(2,77)
DO 93 I=1,NPTS
WRITE(2,88)(XLMND(I),ABSOR(I),OPUT(I),OPAV(I),PHOT(I), + PHOTAV(I),PULN(I),PULAV(I),HVOLT(I))
93 CONTINUE
TYPE 889
999 FORMAT('\nDO YOU WISH TO SAVE THE DECAY DATA?\n')
ACCEPT 91,ANS
IF(ANS.NE.\'Y\')GO TO 970
OPEN(UNIT=3,NAME=\'CHKGPC>DAT\',TYPE=\'NEW\',FORM=\'UNFORMATTED\')
DO 994 I=1,NPTS
WRITE(3) BSX(I),BASE(I),DCX(I),DECMA(I),ABSNOT(I)
994 DO 994 I=1,350
995 WRITE(3) ISPSAV(J,I)
CLOSE(UNIT=3)
890 IF(LMPFLO.EQ.0) WRITE(2,400)
400 FORMAT('C TUNGSTEN LAMP')
IF(LMPFLO.EQ.1) WRITE(2,401)
401 FORMAT('C XENON LAMP')
WRITE(2,97)(GAIN,NSHOT,IFPDAT,ISAMP)
CLOSE(UNIT=2)
95 TYPE 96
96 FORMAT('DO YOU WANT TO OBTAIN ANOTHER SPECTRUM?\n')
ACCEPT 91,ANS
C NEW RETURN STEPPER TO ORIGINAL POSITION
CALL CSSA(16,GR3AD,\'40,G\') \ TURN ON STEPPER POWER AGAIN
KK=TOTSTP(NPARRM)
DO 66 I=1,KKK
CALL CSSA(16,GR3AD,\'240,G\')
CALL CSSA(21,GR3AD,\'200,G\')
66 CALL WAIT(0.0,1)
CALL CSSA(9,GR3AD,D,G) \ TURN OFF STEPPER POWER
IF(ANS.NE.\'Y\')GO TO 9000
STOP
END
ABSCLF. FOR (special)

SUBROUTINE ABSCLF(GAIN, ABSB, PHOTAV, NSHOT)  19-02-92 T. WOODS
C WORKS WITH THE KNOSPC VERSION THAT LETS YOU SAVE DECAY DATA.
COMMON/FINDAB/IDBUF(350), ISAMP, NSK  ! LE CROY DATA
COMMON/EXT/XMIN, BSL, BASEX, DECX
C
C THIS SUBROUTINE FINDS THE MAXIMUM ABSORBANCE AT A GIVEN WAVELENGTH.
NCHIG=2000/ISAMP  ! NO. CHANNELS IGNORED, OP AMP NOT ON YET.
C FIND THE MAXIMUM INTENSITY OF THE DECAY CURVE = MINIMUM IDBUF VALUE.
LITEMP=32767  ! ARBITRARILY LARGE INITIAL VALUE.
SUM=0
IMAX=0  ! THE CH. NO. CORRESPONDING TO THE MINIMUM IDBUF VALUE
DO 60 I=NCHIG+1, 350
IF(IDBUF(I)-IDBUF(I).GE.3*IFIX(SQRT(FLOAT(NSHOT)))) GO TO 60
60
C THE ABOVE IS A TEST TO SEE IF WE'RE ON WELL BEHAVED PART OF THE DECAY
C CURVE.
LITEMP=MIN(IDBUF(I), LITEMP)
IF(LITEMP.EQ.IDBUF(I)) IMAX=I
CONTINUE
XMIN=FLOAT(LITEMP)  ! MAX INTENSITY=MIN IDBUF VALUE IS FOUND.
C NOW FIND THE BASELINE.
DO 70 I=NCHIG+1, IMAX-NSK
SUM=SUM+IDBUF(I)
XSUM=XSUM+FLOAT(XMAX-NCHIG-NSK)  ! BASELINE FOUND
AVEV1=PHOTAV/1000.  ! LIGHT ON PMT OUTPUT IN MILLIVOLTS
VOSCFT=G. /(GAIN*FLOAT(NSHOT))  ! VOLTAGE SCALING FACTOR FOR LE CROY DATA
DIF=BSL-XMIN
ABSB=ALOG10((AVEV1/((AVEV1-(DIF)*VOSCFT))))  ! ABSORBANCE FOUND
BASEX=FLOAT(NCHIG+1)
DECX=FLOAT(IMAX)
RETURN
END
PROGRAM CHKSPC
C THIS PROGRAM TAKES THE UNFORMATTED RT-11 FILE OF DECAY CURVE DATA SAVED
C BY THE SPECIAL VERSION OF KOMSPC. IT WAS TO HAVE THE NAME CHKSPC.DAT.
C (THIS IS DICTATED BY KOMSPC WHICH DOESN'T ALLOW YOU TO CREATE MORE
C THAN ONE FILE OF SAVED DECAY DATA AT A TIME TO DISCOURAGE FILLING OF
C FLOPPY DISCS UNNECESSARILY) IT SHOWS YOU THE INDIVIDUAL DECAY CURVES
C AT EACH WAVELENGTH ALONG WITH THE BASELINE AND DECAY MAXIMUM VALUES
C FOUND BY THE KOMSPC PROGRAM. ALL DATA IS SUMMED AND UNSCALED UNLIKE
C THAT IN LASPHF FOR. BOTH COORDINATES THAT ARE SHOWN WHEN THE BASELINE
C OR DECAY MAXIMUM IS DISPLAYED BY THE GRAPHICS CURSOR ARE IMPORTANT.
C THE MAXIMUM NUMBER OF DECAY CURVES THAT KOMSPC WAS ALLOWED
C TO KEEP IS 15 AND THE DATA THAT IS KEPT IS ONLY THE FIRST 350 POINTS
C OF THE 1024 POINT DECAY CURVE.
C THIS PROGRAM ALSO REQUIRES ANOTHER FILE. IT IS THE FORMATTED FILE
C THAT KOMSPC NORMALLY GIVES AS OUTPUT CONTAINING THE WAVELENGTH.
C ABSORBANCE, PHOTAV, ETC. DATA. THE USER MUST INPUT THE NAME OF THIS
C FILE.
C
C NEEDED SUBROUTINES. CHAPLT.FOR, WAITF, MAC
DIMENSION XLAGDA(80), ABBORB(80), PHOTAV(80), PULEN(80), PULAVE(80),
* BASE(16), DECMAX(16), BSX(16), DCX(16), ABSN(80)
COMMON/ARRAYS/ISPSAV(350, 16)
BYTE Ans, ESC, FILNAM(16)
DATA ESC, "03/
FILNAM(16) = 0.
TYPE 1
1 FORMAT ("FORMATTED FILE INPUT FILENAME:")
ACCEPT 2, (FILNAM(1), I = 1, 15)
2 FORMAT (80A1)
OPEN (UNIT = 2, NAME = FILNAM, TYPE = 'OLD')
READ (2, 3) NPTS
3 FORMAT ("//", 2X, I5)
WRITE (5, *) NPTS
DO 4 I = 1, NPTS
4 READ (2, 5) XLAGDA(I), ABBORB(I), PHOTAV(I), PULEN(I), PULAVE(I)
5 FORMAT (1X, F5.1, 1X, E2, 3.21X, 3(1X, F5.3))
READ (2, 6) GAIN, NSHOTS
6 FORMAT ("//", 7X, F4.1, 7X, I3)
WRITE (5, *) GAIN, NSHOTS
OPEN (UNIT = 3, NAME = 'CHKSPC.DAT', TYPE = 'OLD', FORM = 'UNFORMATTED')
DO 7 I = 1, NPTS
7 READ (3, 8) BSX(I), BASE(I), DCX(I), DECMAX(I), ABSN(I)
DO 7 J = 1, 350
READ (2, 9) ISPSAV(J, I)
CLOSE (UNIT = 2)
CLOSE (UNIT = 3)
IMINT = 10000
IMAX = 10000
DO 100 I = 1, NPTS
TYPE 90, XLAGDA(I)
90 FORMAT ("CURRENT WAVELENGTH = ", F10.1/*DO YOU WISH TO SKIP THIS CURVE?")
ACCEPT 2, ANS
IF (Ans.EQ. 'Y') GO TO 100
DO 8 J = 1, 350
IMINT = IMINT + ISPSAV(J, I)
8 IMAX = MAX (IMAX, ISPSAV(J, I))
IMIN = MIN (IMINT)
IMAX = IMAX
COUNT = I
CALL CHAPLT (COUNT, IMIN, IMAX)
XIMAX = FLOAT(IMAX)
XIMIN = FLOAT(IMIN)
DIFF = XIMAX - XIMIN
C SHOW USER THE BASELINE WITH THE GRAPHICS CURSOR.

20 FORMAT('DATA POINTS: E15.6, X, E15.6)

25 FORMAT('GRAPHICS POINTS: , X , I10)

26 CALL WAIT('O, I, O)

27 FORMAT('RESET TERM. IT HANGS HERE."

28 IF(ANS.LT. 'Y') GO TO 10

C SHOW POINT OF MAXIMUM DECAY TO THE USER WITH THE GRAPHICS CURSOR.

12 IF(ANS.NE. 'Y') GO TO 12

13 FORMAT('DATA POINT: I10, X, E15.6, X, E15.6)

14 IF(ANS.LT. 'Y') GO TO 14

15 CONTINUE

STOP

END
SUBROUTINE CHKPLT(KOUNT, IMIN, IMAX)  ! S-FEB-82
COMMON/ARRAYS/ISPSAV(350, 16)
BYTE ESC
DATA ESC/"33/
TYPE 1, 'a', 'dA'
IDIF=IMAX-IMIN
ILAB=IDIF/5
TYPE 2, '+', ESC, IMIN, IMAX, ILAB, ILAB
2 FORMAT(2A1, 'a d z h 1 i 2 j 9 k 1 I 3 5 0 m . I I 0 , n . I I 0 , + ' 0 S 0 p 0 g . ' I I 0 , r . I I 0 , ' s 0 t 3 5 0 u 0 v 0 w 0 c z ')
CALL WAIT(0, 3, 0)
TYPE 5, '+', ESC
5 FORMAT(2A1, 'U')  NEXT PAGE.
TYPE 6, '+', ESC
9 FORMAT(2A1, 'a a z')  TURNS ON AUTOPLT.
TYPE 4, '+', ESC
4 FORMAT(2A1, 'G')  NEXT LINE PLEASE
DO 100 I=1,350
WRITE(5, 100) I, ISPSAV(I, KOUNT)
100 FORMAT(X, I10, X, I10)
IF(ITTINR()) EG. "32") GO TO 50
TYPE 7, '+', ESC
7 FORMAT(2A1, 'X')  CLEAR LINE ABOVE CURSOR
TYPE 8, '+', ESC
3 FORMAT(2A1, 'A')  MOVE CURSOR UP A LINE
CONTINUE
50 TYPE 80, '+', ESC
RETURN
FORMAT(2A1, 'a b z')  TURN OFF AUTOPLT.
RETURN
END

CHKPLT.FOR plots decay curves observable with CHKSPC.FOR.
PROGRAM LSLMIX

WORKS ON FIXFIT GENERATED LASER FLASH PHOTOLYSIS DATA AND ON DATA
FROM PROGRAMS DERIVED FROM FIXFIT FOR LIKE LASFPH.FOR.

TREACY L. WOODS
JUNE 21, 1982

THIS PROGRAM TAKES FLASH PHOTOLYSIS INTENSITY VS. CHANNEL DATA AND
MAKES THE TRANSFORMATIONS NEEDED TO PERFORM MIXED FIRST AND SECOND
ORDER ANALYSIS BY THE METHOD OF LINSCHITZ AND SARKANEN, JACS, 80: 1938(4826).

NOTES: MATH DERIVATION: SEE WOODS NOTEBOOK II P. 49.
SCHEMATIC OF THE WAY LASER FLASH PHOTOLYSIS DATA FROM THE
MK-11/2 IS OBTAINED TO THE PDP 11/70 FOR USE IN THIS
PROGRAM: SEE WOODS NOTEBOOK III P. 154.
DISCUSSION OF PLOTTING ABILITY OF THIS PROGRAM: SEE
WOODS NOTEBOOK IV P. 296, 167.

ONE OUTPUT FILE IS CREATED CONTAINING:
1. INTENSITY VS. TIME DATA CURVE
2. INTENSITY VS. TIME FIRST ORDER FIT CURVE
3. LN(LOG(ZERO/TRANSMITT)) VS. TIME DATA USED TO DO
THE PURE FIRST ORDER FIT.
4. THE FIRST ORDER FIT FOR #3
5. THE 4TH ORDER FIT FOR #3.
6. THE (SLOPE OF CURVE #5) VS. ABSORBANCE CURVE
7. THE FIRST ORDER FIT OF #6
8. THE INTERCEPT FROM #7 VS. QUENCHER CONCENTRATION
CURVE FOR NO QUENCHER CONCENTRATIONS.
9. THE FIRST ORDER FIT OF #9 WHOSE SLOPE EQUALS THE
QUENCHING RATE CONSTANT.

THE OUTPUT FILE IS SUITABLE FOR GRAPHICAL OBSERVATION AND/OR GENERATION
OF HARD COPY GRAPHS WITH THE USE OF THE HP2648A GRAPHICS TERMINAL AND
J. V. V. KASPER'S PROGRAMS, CILL2MPLP. A COMMAND FILE EXISTS CALLED
VISLIM.COM. IT CAN BE USED WITH AUTPP TO ALLOW "AUTOMATIC" VIEWING
OF ALL THE CURVES IN THE GRAPHICAL OUTPUT FILE FROM THIS PROGRAM.

THE FOURTH ORDER FIT IN THIS PROGRAM IS DONE WITH THE FITTING SUBROUTINES,
POLFIT AND DETEMV USED IN AUTPP WHICH JERRY KASPER GOT FROM BEVINGTON.

FORTRAN SUBROUTINES REFERENCED: MIXLST, POLFIT, DETERM, BIGNO, SMALNO, CURMIX, PLTM1

THIS PROGRAM PLOTS CURVE #6 FOR THE USER AND ALLOWS THE USER TO ENTER
FIT LIMITS WITH A GRAPHICS CURSOR. THEREFORE THIS PROGRAM MUST BE RUN
ON THE HP 2648A GRAPHICS TERMINAL.

PARAMETERS THAT ARE PRINTED OUT IF DESIRED: I-1, NO. OF QUENCHER CONC.

ITEM #4        ITEM#7        ITEM#9
P(I, I)        P(I, 13, I)    P(I, 18, I)  SLOPE
P(2, I)        P(I, 14, I)    P(I, 19, I)  STANDARD DEV. OF SLOPE
P(3, I)        P(I, 15, I)    P(I, 20, I)  INTERCEPT
P(5, I)        P(I, 17, I)    P(I, 22, I)  CORRELATION COEFFICIENT
P10. I, FIRST ORDER LIFETIME P. 7. I, [AMP=HUNDREDSECONDS PER CHANNEL
P10. I, RIGHT FITTING LIMIT CHOSEN VIA TDHND = JJ.
HERE TDHND REFERS TO THE PARENT TDHND, FOR PROGRAM AND ALL OF ITS
DERIVATIVES LIKE FIXGET FOR AND LASFPH FOR.
P12. I, AMPLIFIER GAIN FOR OPA MP = GAIN.
P(23. I) THE QUENCHER CONCENTRATIONS IN MOLES PER LITER.
P(24. I) CHI SQUARE FOR THE FOURTH ORDER FIT.
P(28. I)=A1, P(29. I)=AO WHERE THE FOURTH ORDER FIT IS TO THE POLYNOMIAL:
A4*X^4 + A3*X^3 + A2*X^2 + A1*X + AO

IN THIS PROGRAM, TIME IS HANDLED IN MILLISECONDS. THE TASK FILE IS A
LARGE 87 BLOCKS. CERTAIN ARRAYS LIKE X, Y, AND YCALC ARE USED REPEATEDLY
IN THE PROGRAM TO KEEP THE PROGRAM SIZE DOWN.

MATHEMATICALLY, THE PROGRAM CAN HANDLE DATA FOR UP TO SIX QUENCHER
CONCENTRATIONS. HOWEVER, ONLY THE RESULTS FROM FOUR QUENCHER CONCENTRATIONS
CAN BE PRINTED OUT ON THE 8 1/2 X 11 INCH PAPER NORMALLY USED IN THE
LINE PRINTER. SIX CONCENTRATIONS CAN BE RUN WITH NO PRINT OUT.
A PRINT OUT FOR SIX CONCENTRATIONS CAN BE OBTAINED IF THE PAPER IN
THE LINE PRINTER IS CHANGED TO THE WIDER SIZE.

COMMON/SUBFIT(X(350), Y(350), YCALC(350), W(350), ONEPAR(6)
DIMENSION CF(6)
DIMENSION AB(350), YFIT(350), FX(350), YSAVE(350)
BYTE FILEIN(18), FILOUT(18)
DIMENSION P(30, 6)
BYTE ANB, ESC
BYTE DAII(9)
BYTE INFIL(120)
BYTE SAMP(35)
ESC=’33’
TYPE 888
888 FORMAT(2X, ’CURRENTLY THE ORDER MUST EQUAL 4’,/,
+2X, ’THE MAXIMUM NUMBER OF QUENCHER CONCENTRATIONS IS 6’,/,
+2X, ’ONLY 4 QUENCHER CONC. ALLOWED FOR PRINT OUT ON SMALL PAPER’,/,
+2X, ’ALL DATA IS WEIGHTED EQUALLY’)
TYPE 102
102 FORMAT(’OUTPUT DSN? ’) NAME USER DESIRES FOR GRAPHICAL OUTPUT FILE.
ACCEPT 101; (FILOUT(I), I=1, 17)
FILOUT(I)=0.
OPEN(UNIT=3, TYPE=’NEW’, NAME=FILOUT)
DO 1901 I=1, 20
1901 INFIL(I)=40 PUT SPACES IN INPUT FILE NAMES LABEL FOR PRINT OUT.
NQ=0
1000 TYPE 1111, ’+’, ESC
1111 FORMAT(2A1, ’ d A’) CLEAR GRAPHICS MEMORY
NQ=NQ+1 ’NG IS THE NUMBER OF QUENCHER CONCENTRATIONS.
TYPE 100
100 FORMAT(’INPUT DSN?’)
C THE INPUT FILE IS A FORMATTED FILE IN IAS FORMAT OBTAINED FROM FXWRAC,FOR
C FXFER, AND RTIAS.
ACCEPT 101; (FILEIN(I), I=1, 17)
101 FORMAT (17A1)
FILEIN(I)=0.
OPEN(UNIT=2, TYPE=’OLD’, NAME=FILEIN)
DO 1900 I=1, 10
LAB=20+(NQ-1)*15
INFIL(LAB+I)=FILEIN(I) PUT FILE NAME IN LABEL FOR LATER PRINT OUT.
1900 MARK=LAB+1
DO 1902 I=1, 5
1902 INFIL(MARK(I))=40 PUT SPACES IN THE LABEL. ’40 = SPACE IN OCTAL
READ(2, 105) ISAMP FIND ISAMP FROM THE FRONT PANEL INFO.
READ IT.
105 FORMAT (1X, 14X, I6)
P(7, NQ)=FLDAT(ISAMP)
TYPE 9000, ISAMP SHOW IT TO US FOR VERIFICATION
FORMAT(15X,E15.6)  I1=3*I-1
X11=1
Y(I)=YYV ! SUBSCRIPT Y AS 1, 2, 3, ETC.
(I)=X11*TIMFAC ! 1ST POINT HAS TIME VALUE = ZERO.
FX(I)=X(I) ! SAVE ORIGINAL X VALUES FOR THE OUTPUT FILE.
YSAVE(I)=Y(I) ! SAVE ORIGINAL Y VALUES FOR OUTPUT FILE.
CONTINUE
NXV=341 ! TOTAL NUMBER OF DATA POINTS READ FROM INPUT FILE.
FORMAT(15X,E15.6)  I1=1
X11=1
Y(I)=YYV ! SUBSCRIPT Y AS 1, 2, 3, ETC.
(I)=X11*TIMFAC ! 1ST POINT HAS TIME VALUE = ZERO.
FX(I)=X(I) ! SAVE ORIGINAL X VALUES FOR THE OUTPUT FILE.
YSAVE(I)=Y(I) ! SAVE ORIGINAL Y VALUES FOR OUTPUT FILE.
READ(2,107) VI, GAIN
FORMAT(F10.3, F10.3)  TYPE 9001.VI, GAIN ! SHOW IT TO US FOR VERIFICATION.
FORMAT(15X,E15.6)  I1=1
X11=1
Y(I)=YYV ! SUBSCRIPT Y AS 1, 2, 3, ETC.
(I)=X11*TIMFAC ! 1ST POINT HAS TIME VALUE = ZERO.
FX(I)=X(I) ! SAVE ORIGINAL X VALUES FOR THE OUTPUT FILE.
YSAVE(I)=Y(I) ! SAVE ORIGINAL Y VALUES FOR OUTPUT FILE.
READ(2,111) BSLE, J, JJ
FORMAT(15X,E15.6, F7.2, X, 14, J, 14)  TYPE 9002.BSLE, J, JJ ! SHOW IT TO US FOR VERIFICATION.
FORMAT(15X,E15.6, F7.2, J=J, 'I4', J=J, 'I4')  TYPE 9002.BSLE, J, JJ ! SHOW IT TO US FOR VERIFICATION.
P(1, JQ)=BSLE
P(J, Q)=FLOT(JJ)
CLOSE(J)+2 ! DONE READING INPUT DATA.
RIGHT=J
JLEFT=J
NQP=RIGHT-JLEFT+1 ! NOP IS THE NUMBER OF POINTS TO BE FIT.
FORMAT(15X,E15.6, F7.2, J, JJ)  TYPE 9003.RIGHT, JLEFT ! SHOW US THE RESULTS FOR VERIFICATION.
C CHANGE THE X AND Y INDEXING AGAIN. MAKE POINTS BETWEEN FIT LIMITS
C SUBSCRIPT 1, 2, 3... NOP ALL FITS CAN BE DONE BETWEEN THE SUB-
C SCRIPTS I AND THE NUMBER OF POINTS.
I1=0
DO 1199 I=JLEFT, JRIGHT
I1=I1+1
Y(I1)=Y(I) ! POINTS BETWEEN JLEFT AND RIGHT ARE SET 1, 2, 3... ETC.
C PREPARE DATA FOR FIRST ORDER FIT.
VOGCF=2. /GAIN
DO 110 I=1, NQP
TEMP=BSLE-Y(I)*VOGCF
TEMP=XT-(Y(I)-TEMP)
AB(I)=ALOGIO10(TEMP)
110 Y(I)=ALOGI(AB(I)) ! NOTICE Y(I) NO LONGER HAS THE ORIGINAL DATA.
C DO FIRST ORDER FIT.
LI=1 'SUBROUTINE NUMERICAL INDEXES GIVE ERRORS.
CALL MIXLIST(NQP, LI, NQP)
DO 700 I=1, 5 ! SAVE FIT PARAMETERS.
700 PI(I,JQ)=ONEPAR(I)
DO 811 I=1, NQP
CALL SGMAXN(X, NQP, XM, YMIN) ! FIND EXTREMA
CALL SGMIN(X, NQP, XM, YMIN)
WRITE(3,306) XM, YMIN, YMAX
DO 112 I=1, NQP
811 WRITE(3,106) X(I), Y(I) ! WRITE ITEM #3 IN THE OUTPUT FILE.
WRITE(3,106)
WRITE(3,109)
DO 112 I=1, NQP
WRITE(3,106) X(I), YCALC(I)   ! WRITE ITEM #4 IN OUTPUT FILE.
WRITE(3,108)
WRITE(3,109)

C FIND THE FIRST ORDER CALCULATED DECAY CURVE.
DO 7801 =1, NOP
  TEMP = EXP(YCALC(I))
  TEMP = 10. ** TEMP
  TEMP = TEMP / V1
  TEMP = 1. / TEMP
  TEMP = 1. * TEMP
  YFIT(I) = ((BSLE + VOSCF) - TEMP) / VOSCF
C DO THE 4TH ORDER FIT ON LN(Absorbance) VS. TIME DATA.
  NCF = 5   ! THE NUMBER OF COEFFICIENTS.
  CALL POLFIT(X, Y, NOP, NCF, CF, SIGMA)
  P(24, NQ) = SIGMA   ! SAVE THE CHI SQUARE OF 4TH ORDER FIT.
  P(25, NQ) = CF(5)   ! SAVE THE COEFFICIENTS
  P(26, NQ) = CF(4)
  P(27, NQ) = CF(3)
  P(28, NQ) = CF(2)
  P(29, NQ) = CF(1)
DO 7950 =1, NOP   ! FIND THE CALCULATED 4TH ORDER FIT CURVE.
  Y1 = CF(1)
  Y2 = CF(2) * X(I)
  Y3 = CF(3) * X(I)**2
  Y4 = CF(4) * X(I)**3
  Y5 = CF(5) * X(I)**4
  YCALC(I) = Y1 + Y2 + Y3 + Y4 + Y5   ! NOTE: THE VALUE OF YCALC HAS CHANGED.
DO 113 =1, NOP

113 WRITE(3,106) X(I), YCALC(I)   ! WRITE ITEM #5 IN THE OUTPUT FILE.
WRITE(3,108)
WRITE(3,3100)
  CALL SMALLND(FX, NXY, XMIN)
  CALL SIGNO(FX, NXY, XMAX)
  CALL SMALLND(YSAVE, NXY, YMIN)
  CALL SIGNO(YSAVE, NXY, YMAX)
WRITE(3,2200) XMIN, XMAX, YMIN, YMAX
DO 800 =1, NXY
3200 WRITE(3,106) FX(I), YSAVE(I)   ! WRITE ITEM #1 IN THE OUTPUT FILE.
WRITE(3,108)
WRITE(3,109)
DO 801 =1, NOP
801 WRITE(3,106) X(I), YFIT(I)   ! WRITE ITEM #2 IN THE OUTPUT FILE.
WRITE(3,108)
WRITE(3,3100)
  CALL SMALLND(AB, NOP, XMIN)
  CALL SIGNO(AB, NOP, XMAX)
  CALL SMALLND(Y, NOP, YMIN)
  CALL SIGNO(Y, NOP, YMAX)
WRITE(3,3200) XMIN, XMAX, YMIN, YMAX
DO 115 =1, NOP
  X(I) = AB(I)   ! X(I) NOW IS THE ABSORBANCE.
  WRITE(3,106) AB(I), Y(I)   ! WRITE ITEM #6 IN OUTPUT FILE.
WRITE(3,108)
WRITE(3,109)

C NOW FIT THE SLOPE VS. ABSORBANCE DATA.
  CALL PLTMIX(1, NOP, X, Y, XMIN, XMAX, YMIN, YMAX, 0.)   ! PLOT IT FIRST
CALL CURIMIX(XLT, YLT, YRT, XRT, XMIN, YMIN, YMAX) ! WE CHOOSE FIT LIMITS.
TYPE = XLT, YLT, YRT, XMIN, YMIN, YMAX) ! SHOW US FIT LIMITS IN DATA UNITS.
DO 904 I=1, NP
  XLDIF=ABS(XLT-X(I))
  YLDIF=ABS(YLT-Y(I))
  XLCHK=ABS(.02*XLT)
  YLCHK=ABS(.02*YLT)
  ILEFT=1
  IF((XLDIF .LE. XLCHK) .AND. (YLDIF .LE. YLCHK)) GO TO 905
CONTINUE
905 LLT=LEFT ! LLT=SUBSCRIPT VALUE FOR THE LEFT LIMIT
  XRDIF=ABS(XRT-X(I))
  YRDIF=ABS(YRT-Y(I))
  XRCCH=ABS(XRT*02)
  YRCCH=ABS(YRT*02)
  IRIGHT=1
  IF((XRDIF .LE. XRCCH) .AND. (YRDIF .LE. YRCCH)) GO TO 907
CONTINUE
907 LRT=RIGHT ! LRT=SUBSCRIPT VALUE FOR RIGHT LIMIT
  TYPE 3313-LLT, LRT ! SHOW US RESULTS FOR VERIFICATION
3313 FORMAT((I4, X, I4))
  NNP=ABS(LLT-LRT)+1 ! NNP IS NUMBER OF POINTS TO BE FIT.
  CALL MIXLST(NNP, LRT, LLT) ! RIGHT TO LEFT, YES. SINCE LRT<LLT
  CALL PLTMIX(LRT, LLT, X, YCALC, XMIN, XMAX, YMIN, YMAX, 1.) ! PLOT FIT CURVE.
  TAUINT=1000. ! ONEPAR(3) : LIFETIME IN MICROSEC BASED ON L&G INTERCEPT.
  TYPE 4445. ! ONEPAR(3)
  FORMAT(18, ANS)
  IF(ANS.EQ.'Y') GO TO 4444
  DO 116 I=LRT, LLT
  WRITE(3,108) X(I), YCALC(I) ! WRITE ITEM #7 IN OUTPUT FILE.
WRITE(3,108)
  WRITE(3,3100)
  DO 950 I=13,17 ! SAVE FIT PARAMETERS
  P(I, NQ)=ONEPAR(I-12)
  TYPE 119
950 FORMAT('WHAT IS THE QUENCHER CONCENTRATION IN MOLES PER LITER?')
  ACCEPT = P(23, NQ)
  TYPE 117
117 FORMAT('DO YOU WISH TO DO ANOTHER QUENCHER CONCENTRATION?')
  ACCEPT=ANS
  TYPE 118
118 FORMAT(A1)
  IF(ANS.EQ.'Y') GO TO 1000
  IF(NG .EQ. 0) GO TO 2010
  TYPE 120-P(23, NQ), P(13, NQ)
120 FORMAT('FOR QUENCHER CONCENTRATION', E3, 'MOLES PER LITER', E5, 'THE FIRST ORDER COMPONENT IS', E15.6, 'THE SECOND ORDER COMPONENT IS', E15.6)
  GO TO 3000
2010 DO 2000 I=1, NG
  X(I)=P(23, I) ! THE X VALUES ARE NOW QUENCHER CONCENTRATIONS
2000 Y(I)=P(13, I)+1 ! THE Y VALUES ARE NOW FIRST ORDER COMPONENTS.
  CALL SMALNO(X, NG, XMIN) ! FIND EXTERA
  CALL BIGNO(X, NG, XMAX) ! CALL BIGNO(Y, NG, YMIN)
  WRITE(3,3200) XMIN, XMAX, YMIN, YMAX
  DO 2020 I=1, NG
2020 WRITE(3,106) X(I), Y(I) ! WRITE ITEM #8 IN THE OUTPUT FILE.
WRITE(3,108)
WRITE(3,109)
C FIT QUENCHER CONCENTRATION VS. FIRST ORDER COMPONENT DATA
CALL MIXLST(NG, L1, NQ)
DO 6900 I=18, 22 ! SAVE FIT PARAMETERS.
6900 P(I,1)=ONEPAR(I-17)
DO 2002 I=1, NG
WRITE(3,106) X(I), YCALC(I) 'WRITE ITEM #9 IN OUTPUT FILE.
TYPE 2003, NG,P(18.1),P(20.1)
FORMAT(1 FOR 14, 'QUENCHER CONCENTRATIONS' ' , THE QUENCHING
+ RATE CONSTANT IS ' ,E15.6 , ' , THE OTHER FIRST ORDER COMPONENTS
+ ARE ' ,E15.6 )
TYPE 2004
FORMAT(' WOULD YOU LIKE A PRINT OUT OF PERTINENT PARAMETERS')
ACCEPT 118, ANS
IF(ANS.EQ. 'N') GO TO 5000
IF(ANS.NE. 'Y') GO TO 3000
TYPE 2006
FORMAT(5S1) 'SAMPLE ID'
ACCEPT 2007, (SAMPID(I), I=1,55)
FORMAT(55A1)
CALL DATE(DA1T)
PRINT 6025
FORMAT(' PROGRAM LSMIX.FTN')
PRINT 6026, (D1AT(I), I=1,9)
FORMAT(4, I, 9A1)
PRINT 2008, (SAMPID(I), I=1,55)
FORMAT(' THE SAMPLE ID IS: ' ,55A1)
PRINT 2009, (FILOUT(I), I=1,17)
FORMAT(' THE NAME OF THE OUTPUT GRAPHICS FILE IS: ' ,17A1)
PRINT 6000, (P(23.1), I=1,49)
FORMAT(5 ' QUENCHER CONC M/LI ' ,6(1PE12, 5.3X))
PRINT 6027, (INFILB(I), I=1,120)
FORMAT(120A1)
PRINT 6027
FORMAT(5 ' LN(LOG(V1/(V1-0V))) FIT PARAMETERS', ')
PRINT 6002, (P(1.1), I=1,NG)
FORMAT(' SLOPE , 14X , 6(1PE12, 5.3X)')
PRINT 6003, (P(2.1), I=1,NG)
FORMAT(' SD SLOPE , 1X , 6(1PE12, 5.3X)')
PRINT 6004, (P(3.1), I=1,NG)
FORMAT(' INTERCEPT , 10X , 6(1PE12, 5.3X)')
PRINT 6005, (P(4.1), I=1,NG)
FORMAT(' SDINTERCEPT , BX , 6(1PE12, 5.3X)')
PRINT 6006, (P(5.1), I=1,NG)
FORMAT(' CORCO , 14X , 6(E12, 5.3X)')
PRINT 6007, (P(6.1), I=1,NG)
FORMAT(' FIRST ORDER TAU' ,4X , 6(1PE12, 5.3X))
PRINT 6008
FORMAT(' SLOPE OF LN(LOG(V1/(V1-0V)) VS. ABSORBANCE FIT
+ PARAMETERS', ')
PRINT 6002, (P(13.1), I=1,NG)
PRINT 6003, (P(14.1), I=1,NG)
PRINT 6004, (P(15.1), I=1,NG)
PRINT 6005, (P(16.1), I=1,NG)
PRINT 6006, (P(17.1), I=1,NG)
PRINT 6009, (P(24.1), I=1,NG)
FORMAT(' CHI SQ ORDER 4 FIT ' ,6(1PE12, 5.3X), ')')
PRINT 6018
FORMAT(' FOURTH ORDER FIT COEFFICIENTS', ')
PRINT 6019, (P(25.1), I=1,NG)
FORMAT(' A4 , 17X , 6(1PE12, 5.3X)')
PRINT 6020, (P(26.1), I=1,NG)
FORMAT(' A3 , 17X , 6(1PE12, 5.3X)')
PRINT 6021, (P(27.1), I=1,NG)
FORMAT(' A2 , 17X , 6(1PE12, 5.3X)')
PRINT 6022, (P(28.1), I=1,NG)
FORMAT(' A1 , 17X , 6(1PE12, 5.3X)')
PRINT 6023, (P(29.1), I=1,NG)
FORMAT(' A0 , 17X , 6(1PE12, 5.3X)')
IF(NG,NQ, GO TO 601
PRINT 6019
FORMAT(/, 'QUENCER CONCENTRATION VS. K1 FIT PARAMETERS', /)
PRINT 6002, P(I8, 1)
PRINT 6003, P(I9, 1)
PRINT 6004, P(I20, 1)
PRINT 6005, P(I21, 1)
PRINT 6006, P(I22, 1)
PRINT 6012, (P(7, I), I=1, NG)
FORMAT(/, 'NANOSECOND PER CHAN., 2X, 6(F12.0, 3X))
PRINT 6013, (P(8, I), I=1, NG)
FORMAT(' BASELINE', I1X, 6(F12.2, 3X))
PRINT 6014, (P(9, I), I=1, NG)
FORMAT(' LEFT LIMIT', 9X, 6(F12.0, 3X))
PRINT 6015, (P(10, I), I=1, NG)
FORMAT(' RIGHT LIMIT', 9X, 6(F12.0, 3X))
PRINT 6016, (P(11, I), I=1, NG)
FORMAT(' V1', 17X, 6(SX, F3.0, 5X))
PRINT 6017, (P(12, I), I=1, NG)
FORMAT(' AMPLIFIER GAIN', 5X, 6(SX, F4.0, 6X))
CLOSE(UNIT=3)
STOP
END

SUBROUTINE SIGNO(X, N, BIG)
DIMENSION X(N)
C THIS SUBROUTINE FINDS THE MAXIMUM VALUE OF A REAL ARRAY OF SIZE, N.
TEMP=-1. E26
DO 10 I=1, N
TEMP=MAX1(TEMP, X(I))
10 BIG=TEMP
RETURN
END

SUBROUTINE SMALLNO(X, N, SMALL)
DIMENSION X(N)
C THIS SUBROUTINE FINDS THE MINIMUM VALUE OF A REAL ARRAY OF SIZE, N.
TEMP=1. E26
DO 20 I=1, N
TEMP=MIN1(TEMP, X(I))
20 SMALL=TEMP
RETURN
END
SUBROUTINE CURMIX(XLT, YLT, XRT, YRT, XMIN, YMIN, XMAX, YMAX)
C FINDS X COORDINATES FOR MIXED ORDER FITTING LIMITS.
BYTE ESC, ANS
ESCC='33
TYPE 1, ' ', ESC
1 FORMAT(2A1, '*dK') ! TURN ON GRAPHICS CURSOR.
10 TYPE 3
3 FORMAT(' POSITION THE CURSOR ON THE LEFT LIMIT')
TYPE 4
4 FORMAT(' IS THE CURSOR PROPERLY POSITIONED??')
ACCEPT 5, ANS
5 FORMAT(A1)
TYPE 6, ' ', ESC
6 FORMAT(2A1, '*dG') ! READ CURSOR POSITION
TYPE 7, ' ', ESC
7 FORMAT(2A1, 'g') ! RESET TERMINAL
ACCEPT 8, LX, LY ! LX AND LY ARE CURSOR COORD IN GRAPHICS UNITS
8 FORMAT(1E, X, I6)
XDELTA=XMAX-XMIN
YDELTA=YMAX-YMIN
FACTOR=XDELTA/0.14.
YFACTOR=YDELTA/30.4.
XLT=FLOAT(LX-70)+FACTOR*XMIN
YLT=FLOAT(LY-45)+YFACTOR+YMIN
TYPE 15, XLT, YLT
15 FORMAT(' IN DATA UNITS.  X = ',E13.6, '  Y = ',E13.6)
9 TYPE 13
13 FORMAT(' POSITION THE CURSOR ON THE RIGHT LIMIT')
TYPE 11
11 FORMAT(' IS THE CURSOR PROPERLY POSITIONED??')
ACCEPT 5, ANS
IF(ANS.NE.'Y') GO TO 9
TYPE 6, ' ', ESC
TYPE 7, ' ', ESC
ACCEPT 9, LX, LY
XRT=FLOAT(LX-70)+FACTOR*XMIN
YRT=FLOAT(LY-45)+YFACTOR+YMIN
TYPE 13, XRT, YRT
13 TYPE 16
16 FORMAT(' DO YOU WANT TO CONTINUE??')
ACCEPT 5, ANS
IF(ANS.NE.'Y') GO TO 17
TYPE 12, ' ', ESC
12 FORMAT(2A1, '*dL') ! TURN THE CURSOR OFF.
RETURN
END
C FUNCTION DETERM /V001A/ 2/13/78

PURPOSE.
CALCULATE THE DETERMINANT OF A SQUARE MATRIX

USAGE:
DET = DETERM (ARRAY, NORDER)

PARAMETERS:
ARRAY = MATRIX
NORDER = ORDER OF DETERMINANT (DEGREE OF MATRIX)

SUBPROGRAMS REQUIRED:
NONE

COMMENTS.
THIS SUBPROGRAM DESTROYS THE INPUT MATRIX ARRAY
DIMENSION STATEMENT VALID FOR NORDER UP TO 5

PROGRAM IS ON PAGE 294 OF P. R. BEVINGTON.
"DATA REDUCTION AND ERROR ANALYSIS FOR THE PHYSICAL
SCIENCES"

FUNCTION DETERM(ARRAY,NORDER)

DOUBLE PRECISION ARRAY, SAVE
DIMENSION ARRAY(3,3)

10 DETERM=1.
11 DO 50 K=1,NORDER
12
C INTERCHANGE COLUMNS IF DIAGNOL ELEMENT IS ZERO
C
21 IF (ARRAY(K,K),NE 0) GO TO 41
22 DO 23 J=1,K-1
23 IF (ARRAY(K,J),NE 0) GO TO 31
24 CONTINUE
25 DETERM=0.
26 GO TO 50
31 DO 34 I=K,NORDER
32 SAVE=ARRAY(I,J)
33 ARRAY(I,J)=ARRAY(I,K)
34 ARRAY(I,K)=SAVE
35 DETERM=-DETERM

C SUBTRACT ROW K FROM LOWER ROWS TO GET DIAGONAL MATRIX
C
41 DETERM=DETERM*ARRAY(K,K)
42 IF (K.GE. NORDER) GO TO 50
43 K=K+1
44 DO 46 I=K+1,NORDER
45 ARRAY(I,J)=ARRAY(I,J)-ARRAY(I,K)*ARRAY(K,J)/ARRAY(K,K)
46 CONTINUE
47 CONTINUE
50 RETURN
END

DETERM.FTN is required by POLFIT.FTN.
SUBROUTINE MIXLST(N,L,M)

THIS SUBROUTINE DOES FIRST ORDER LEAST SQUARES FITTING. IT IS
COMPATIBLE WITH THE PROGRAM MIXFIT.FTN. (Also LAHIX.FTN.
N=NUMBER OF POINTS BEING FIT
L=RIGHT LIMIT OF FIT
M=LEFT LIMIT OF FIT

ONEPAR(1) = SLOPE
2 STANDARD DEVIATION OF THE SLOPE
3 INTERCEPT
4 STANDARD DEVIATION OF THE INTERCEPT
5 CORRELATION COEFFICIENT

COMMON/ Subfit/x(350), y(350), ycalc(350), w(350), onepar(6)
S1=0.
S2=0.
S3=0.
S4=0.
S5=0.
DO 50 I=L,M
  S1=S1+(Y(I)*X(I))
  S2=S2*X(I)
  S3=S3+Y(I)
  S4=S4+(X(I))**2
  S5=S5+Y(I)*Y(I)
50
ZN=N
DENOM=(ZN+S4)-(S2**2)
ONEPAR(1)=(N*N*I-1)*S2+S3)/DENOM
ONEPAR(2)=(3-ONEPAR(1)*S2)/ZN
RESID=O
DO 60 J=L,M
  YCALC(J)=ONEPAR(3)+ONEPAR(1)*X(J)
60
RESID=RESID+(Y(J)-YCALC(J))**2
SIG=RESID/(IN-2)
ONEPAR(4)=SQR(TSIG2+SIG)/DENOM
ONEPAR(5)=SQR(TSIG2+IN)/DENOM
SX=SQR(TABS(SIG2-SIG2)/IN/(IN-1))
SY=SQR(TABS(SIG2-SIG2)/IN/(IN-1))
ONEPAR(6)=(S1-S2*S3)/IN/(IN-1)*SX*SY
RETURN
END
PLTMIX.FTN

SUBROUTINE PLTMIX(LIMR, LIML, R, S, XMIN, XMAX, YMIN, YMAX, PLTFLG)
DIMENSION R(350), S(350)
BYTE ESC
ESC='33'
NQP=1ABS(LIMR-LIML)+1
IF(PLTFLG.EQ.0) GO TO 1000
LINT=1
GO TO 900
1000 LINT=9
900 XMARK=(XMAX-XMIN)*2
YMARK=(YMAX-YMIN)*2
TYPE 2, '+' , ESC , LINT , XMIN , XMAX
FORMAT(2A1,'e d 2h 11 $2.0 ', 14 , 'k ' , E15.6 , ' ' , E15.6 , ' ' , m )
TYPE 30, YMIN, YMAX, XMARK, XMARK
FORMAT(E15.6 , 'n ' , E15.6 , 'o ' , E15.6 , 'p ' , E15.6 , 'q ' )
TYPE 31, YMARK, YMARK, NQP
FORMAT(E15.6 , '+ ' , E15.6 , 'G t ', I4 , 'u 0v 0w c Z ' ) ! FILL MENU.
CALL WAIT(3, 2, M) ! SLOW DOWN, GET SET.
TYPE 5, '-' , ESC
5 FORMAT(2A1, 'U') ! NEXT PAGE.
4 FORMAT(2A1, ' A') ! TURN AUTOPLOT ON.
6 FORMAT(2A1, 'S') ! NEXT LINE
DO 150 I=LIML, LIMR ! SEND DATA
150 FORMAT(3, 100) R(I), S(I)
100 FORMAT(E15.6, X15.6)
TYPE 7, '-' , ESC
7 FORMAT(2A1, 'K') ! CLEAR LINE ABOVE CURSOR.
TYPE 8, '+' , ESC
8 FORMAT(2A1, 'A') ! MOVE CURSOR UP A LINE. WRITE NEXT POINT IN SAME SPOT.
150 CONTINUE
TYPE 80, '+' , ESC
80 FORMAT(2A1, 'A b Z') ! TURN AUTOPLOT OFF
RETURN
END

PLTMIX.FTN plots curves generated by LSMIX.FTN on the HP2648A graphics terminal.
SUBROUTINE POLFIT

PURPOSE:
MAKE A LEAST-SQUARES FIT TO DATA WITH A POLYNOMIAL CURVE
Y = A(1) + A(2)*X + A(3)*X^2 + A(4)*X^3 + ...

USAGE:
CALL POLFIT(X, Y, NPTS, NTERMS, A, CHISQR)

PARAMETERS:
X = ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
Y = ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
NPTS = NUMBER OF PAIRS OF DATA POINTS
NTERMS = NUMBER OF COEFFICIENTS (DEGREE OF POLYNOMIAL + 1)
A = ARRAY OF COEFFICIENTS OF POLYNOMIAL
CHISQR = REDUCED CHI SQUARE FOR FIT

SUBROUTINES REQUIRED:
DETERM(ARRAY, NORDER)
EVALUATES THE DETERMINANT OF A SYMMETRIC TWO-DIMENSIONAL
MATRIX OF ORDER NORDER

COMMENTS:
DIMENSION STATEMENT VALID FOR NTERMS UP TO 5

PROGRAM MODIFIED FROM THAT ON PAGE 140 OF
P. R. BEVINGTON, "DATA REDUCTION AND ERROR ANALYSIS FOR THE
PHYSICAL SCIENCES"

SUBROUTINE POLFIT(X, Y, NPTS, NTERMS, A, CHISQR)

DOUBLE PRECISION SUMX, SUMY, XTERM, YTERM, ARRAY, CHISQ
DIMENSION X(1), Y(1), A(1)
DIMENSION SUMX(9), SUMY(5), ARRAY(5, 5)

ACCUMULATE SUMS
11 NMAX=2*NTERMS-1
DO 13 N=1, NMAX
13 SUMX(N)=0
DO 15 J=1, NTERMS
15 SUMX(J)=0
CHISQ=0
21 DO 50 I=1, NPTS
23 XI=X(I)
25 YI=Y(I)
27 XTERM=1
DO 44 N=1, NMAX
29 SUMX(N)=SUMX(N)+XTERM
31 XTERM=XTERM*XI
33 YTERM=YI
DO 48 N=1, NTERMS
35 SUMY(N)=SUMY(N)+YTERM
37 YTERM= YTERM*XI
40 CHISQ=CHISQ+YI*YI
50 CONTINUE
CONSTRUCT MATRICES AND CALCULATE COEFFICIENTS

DO 54 J=1, NTERMS
    DO 54 K=1, NTERMS
      N=J+K-1
      ARRAY(J, K)=SUMX(N)
 54  IF (DELTA .NE. 0.0) GO TO 61
      RISGR=0.
      DO 59 J=1, NTERMS
        A(J)=0.
        GO TO 80
 59    DO 70 L=1, NTERMS
 60    DO 66 J=1, NTERMS
        N=J+K-1
      ARRAY(J, K)=SUMX(N)
      ARRAY(J, L)=SUMY(J)
      A(L)=DETERM(ARRAY, NTERMS)/DELTA
      CALCULATE CHI SQUARE

DO 75 J=1, NTERMS
 76           CHISQ=CHISQ+2.0*A(J)*SUMY(J)
      DO 75 K=1, NTERMS
        N=J+K-1
      CHISQ=CHISQ+A(J)*A(K)*SUMX(N)
      FREE=NPTR-TERMS
      CHISQR=CHISQ/FREE
      IF (FREE .EQ. 0.0) GO TO 37
 80 RETURN
END

POLFIT.FTN is used by LSMIX.FTN to obtain the fourth order fit parameters for the InA vs. time curve. These parameters lead to a value for the slope of the curve. A plot of slope vs. absorbance is needed for the Linschitz and Sarkany mixed first and second order data analysis. POLFIT.FTN uses a matrix method and requires the subroutine DETERM.FTN. Both POLFIT.FTN and DETERM.FTN were obtained from Dr. J. V. V. Kasper's program AUTOAPP.FTN.
This is an example of LSMIX.FTN printed output.

PROGRAM LSMIX.FTN

23-JUN-82
THE SAMPLE ID IS: p-METHACETOPHEN + 2.3-DIOXA-1,1,4,4-4-TETRAMETHYLCYCLOHEXANE
THE NAME OF THE OUTPUT GRAPHICS FILE IS: FOUR.GPH

QUENCHER CONC M/LI 0.00000E-01 7.75000E-03 2.03000E-02 3.37000E-02

21JUN3.MIX 21JUN4.MIX 21JUN5.MIX 21JUN6.MIX

LN(LOG(V1/V1-DV)) FIT PARAMETERS

SLOPE m/sec^-1 -5.57700E+01 -8.69416E+01 -1.29943E+02 -1.69985E+02
SD SLOPE 3.04483E+01 6.25607E+01 1.18214E+02 1.73444E+02
INTERCEPT -2.14730E+00 -1.98306E+00 -1.72183E+02 -1.52499E+02
SDINTERCEPT 1.33136E-02 1.50567E-02 2.40683E-02 3.07698E-02
CORCO -0.99109E+00 -0.99565E+00 -0.99438E+00 -0.99433E+00
FIRST ORDER TAU m/sec -1.76115E+01 1.15020E+01 7.69535E+00 5.88446E+00

SLOPE OF LN(LOG(V1/V1-DV)) VS. ABSORBANCE FIT PARAMETERS

SLOPE -1.03255E+03 -1.07984E+03 -1.56236E+03 -2.27518E+03
SD SLOPE 3.89483E+00 7.46741E+00 1.91899E+01 5.24628E+01
INTERCEPT 2.58143E+01 6.45347E+01 1.07145E+02 1.42496E+02
SDINTERCEPT 1.85132E+01 2.36104E+01 4.98198E+01 1.06308E+00
CORCO -0.99921E+00 -0.99694E+00 -0.99513E+00 -0.98595E+00

CHI SQ ORDER 4 FIT 4.58934E-04 8.97503E-04 2.41318E-03 2.61162E-03

FOURTH ORDER FIT COEFFICIENTS

A4 1.38997E+06 1.03892E+04 2.64621E+06 4.28132E+06
A3 -1.56923E+05 -1.29838E+03 -2.60312E+05 -3.79070E+05
A2 7.33959E+03 5.34094E+03 1.01032E+04 1.49006E+04
A1 -2.06833E+02 -2.29129E+02 -3.71472E+02 -4.39120E+02
A0 -1.09024E+00 -9.42980E+00 -9.27008E+00 5.41681E+02

QUENCHER CONCENTRATION VS. k1 FIT PARAMETERS

SLOPE 3.40340E+03 m/sec^-1 M^-1 h^-1 5.90*10^6 L/msec
SD SLOPE 3.16760E+02
INTERCEPT 3.24746E+01
SDINTERCEPT 6.32888E+00
CORCO 0.99151E+00

NANOSEC PER CHAN 50. 50. 50. 50.
BASELINE -9.22 35.46 5.38 11.29
LEFT LIMIT 61. 88. 61. 61.
RIGHT LIMIT 270. 239. 199. 198.
V1 1597. 1779. 1919. 2250.
AMPLIFIER GAIN 1. 1. 1. 1.
LSWRFM.FOR

BYTE DAI(9), THME(8)
BYTE ID(40)
BYTE OUTNM(16)
DIMENSION ONEPAR(6), ORIGDT(341)
BYTE FILNM(16)

200 TYPE 2
2 FORMAT(‘*FILNM IN’)
   IFFITTIN(). EQ. ‘32’ GO TO 100
   ACCEPT 1, (FILNM(I), I=1, 12)
1 FORMAT(12A1)
   FILNM(16)=0.
   OPEN(UNIT=1, NAME=FILNM, TYPE=’OLD’, READONLY, DISP=’SAVE’,
      + FORM=’UNFORMATTED’)
   READ(1, END=20, ERR=20) ID
   READ(1, END=20, ERR=20) DAI, THME
   READ(1, END=20, ERR=20) IDIFLg
   READ(1, END=20, ERR=20) IFF, IPRTR, ISAMP, IATTN
   READ(1, END=20, ERR=20) ORIGDT
   READ(1, END=20, ERR=20) V1, GAIN, SLITEN, SLITEX
   READ(1, END=20, ERR=20) (ONEPAR(I), I=1, 6)
   READ(1, END=20, ERR=20) ABSMAX
   READ(1, END=20, ERR=20) BSLE, J, JJ
   close(UNIT=1)
   TYPE 8800
8800 FORMAT(‘*OUTPUT FILENAME’)
   Accept 8900, (OUTNM(I), I=1, 12)
8900 FORMAT(12A1)
   OUTNM(16)=0.
   OPEN(UNIT=2, NAME=OUTNM, TYPE=’NEW’, DISP=’SAVE’,
      + FORM=’FORMATTED’)
   WRITE(2, 5001) ID
5001 FORMAT(40A1)
   WRITE(2, 5000) DAI, THME
5000 FORMAT(9A1, X, 8A1)
   WRITE(2, 4000) IDIFLg
   WRITE(2, 6000) IFF, IPRTR, ISAMP, IATTN
6000 FORMAT(4(I6, X))
4000 FORMAT(I4)
   DO 15 I=1, 341
   WRITE(2, 10) I, ORIGDT(I)
10 FORMAT(I4, X, E15. 6)
15 CONTINUE
   WRITE(2, 5002) V1, GAIN, SLITEN, SLITEX
5002 FORMAT(4F10. 3)
   WRITE(2, 1000) (ONEPAR(I), I=1, 6)
1000 FORMAT(6(E15. 6, X))
   WRITE(2, 2000) ABSMAX
2000 FORMAT(F7. 4)
   WRITE(2, 2500) BSLE, J, JJ
2500 FORMAT(F7. 2, X, I4, X, I4)
   close(UNIT=2)
   GO TO 200
20 TYPE 25
25 FORMAT(‘ERROR DURING READ’)
100 STOP
END

LSWRFM.FOR reads unformatted files generated by LASFPH.FOR and writes out formatted data files which are suitable for transfer to the PDP 11/70 via FXFER where the formatted files can be used by the program LSMIX.FTN.
REFERENCES

6. My calculation from his data.
20. This assumes that $k_2$ for toluene is one seventh of the value found for cyclohexene.


46. See reference 44 p. 67.


57. by Mr. Dalen Keys, this laboratory.


60. Adam, W. "Safety Measures for Handling Concentrated Hydrogen Peroxide", private communication to Dr. Engel.

61. Dr. C. Hobbs, Celanese Chemical Corp. private communication.


65. See reference 64.


74. We are grateful to Dr. Ronald J. Parry for a sample of Adams catalyst.


79. We are grateful to Dr. Ronald J. Parry for a sample of methylene blue hydrochloride.


85. Determined by Mr. Douglas W. Horsey by actinometry in this lab.


85. Determined by Mr. Douglas W. Horsey by actinometry in this lab.


