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PART I: A SEMI-AUTOMATIC SYSTEM FOR
QUANTITATIVE SOLUTION PREPARATION. PART
II: TRIPHENYLMETHYL: DISSOCIATION
EQUILIBRIUM AND REACTION WITH THIOPHENOL.

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PART I: A SEMI-AUTOMATIC SYSTEM FOR QUANTITATIVE SOLUTION PREPARATION

PART II: TRIPHENYLMETHYL: DISSOCIATION EQUILIBRIUM AND REACTION WITH THIOPHENOL

BY

Peyton Scott Glaspie

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

Doctor of Philosophy

Thesis Director's Signature:

Houston, Texas
April, 1974
DEDICATION

To my Grandparents, D. R. and Mary Scott
ACKNOWLEDGEMENTS

I wish to express my appreciation to Professor Edward S. Lewis for his guidance, inspiration and patience during the course of this work. Financial support by the Rice University and the Robert A. Welsh Foundation is gratefully acknowledged.

Thanks are also due to George Zivley for his patient personal instruction in the principles of electronics. R. E. Maxwell gave much helpful advice in mechanical design and construction during this work and his efforts were heartily appreciated.

Special thanks are due to my understanding and hard-working wife, Nancy, not only for her assistance in the preparation of this manuscript, but also for her encouragement and devotion. I also thank Don Burkhart for his help in preparing the manuscript drawings and diagrams.

Finally, I wish to express my love and gratitude to my parents for their understanding, support, and advice at times when it was most needed.
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Appendix
PART I

A SEMI-AUTOMATIC SYSTEM FOR QUANTITATIVE SOLUTION PREPARATION
INTRODUCTION

The preparation of liquid samples has involved many manual and repetitive operations on the part of the chemical investigator. Such sample preparations are often limited in precision by the investigator's ability to repeat exactly each one of several demanding manual operations. Such repetitive operations often foster procedural errors attributable to boredom. This type of work is often encountered in physical-organic chemistry in connection with rate measurements and equilibrium determinations. Such endeavors usually involve preparing a large number of samples of varying concentrations and subjecting these to an analytical procedure, often repetitively, to determine time dependence.

With the advent of sophisticated electromechanical techniques, it has become possible to construct an instrument capable of performing liquid sample preparations semi-automatically. Such an instrument allows the chemist to employ his time in interpreting data obtained from experiments by relieving him of much of the repetitive sample preparation tedium. This instrument gives good precision in liquid sample preparations and thereby yields high quality data obtained from measurements involving these samples.

This work deals with the design, construction and testing of a device capable of semi-automatic preparation of two-component liquid samples. The design used is basically that of a commercially available device, the Ultraburet Model 200 by Scientific Industries. This device uses a precision micrometer screw to drive a piston. This
piston displaces the liquid to be delivered. The exact volume displaced is given by a calibrated wheel attached to the drive screw. Each revolution of the piston drive screw causes the piston to displace a volume of liquid. The number of revolutions is thus a measure of the total volume delivered. If each revolution is divided into one hundred equal rotational increments, then each increment will likewise be a direct measure of the volume delivered. By counting the number of rotational increments, the volume delivered may be determined. In the device constructed, each rotational increment is counted electronically. The total number of accumulated counts is compared to a preset value. If this number of accumulated counts is smaller than the preset value, delivery is continued, otherwise delivery is halted. In order to refill this device, it must be connected to some type of liquid reservoir by means of a valve and then the drive motor reversed. When another delivery is to be made, the device must again be connected to the delivery point. These operations are performed electronically in the present system to further minimize the need for operator attention.

Several factors must be considered with regard to the precision of a liquid delivery system of this type. Obviously, the component parts of the system must be of rigid construction to minimize errors arising from flexion and consequent volume changes. A problem in any measuring system also arises from temperature variations. Such variations not only cause the delivered liquid to change volume but also cause the system to change volume. This leads to inaccuracies which may be minimized by rigid construction of system components and by careful temperature regulation of the system, but cannot be entirely avoided. Other design considerations must be simplicity of utilization, reliability of components, and ease of servicing. It is believed that
the system in its present form embodies all three of these concepts. Safety circuits have been included which prevent the system from damaging itself as the result of an incorrect instruction from the operator. All circuits have been constructed using electronic techniques rather than mechanical devices when possible. Where possible, parts have been chosen for wide availability. Where commercial devices were not available, parts were constructed in the simplest manner that would still insure good performance.

A system capable of delivering precise and accurate volumes of liquid reagents must be monitored by devices capable of converting volume measurements to easily readable form. A practical approach is found in the field of digital electronics. Digital electronics deals with the counting of integers and so may be directly applied to accumulating the rotational screw increments mentioned previously. The volume of liquid delivered may then be determined directly from the number of counts accumulated. Although digital electronics is based on binary operations, a decimal presentation was chosen for the reason that it is much easier to interpret than a binary readout.

As mentioned previously, the volume delivered by the system is divided into increments. The smaller the size of the increments, the higher is the potential precision of delivery of the system. The modified commercial unit may deliver up to six milliliters with each increment representing one microliter. The unit of original design may deliver up to twenty milliliters with each increment representing 3.6 µl.

John Bartmess has previously constructed a motorized delivery system. Several problems were associated with the utilization of that device. The counter used was a binary device necessitating the
troublesome task of binary to decimal conversion by the operator. The system had to be manually connected to the reservoir or to a delivery tip and manually switched for the refill operation. These drawbacks have been eliminated in the system herein described.
DESCRIPTION

**General Operating Principles**

The mechanical portions of this device (Figures 1 and 2) consist of two syringes driven by reversible electric motors by means of precision screws. In each of these devices, a precisely machined piston is used to displace a liquid reagent. The pistons are driven by precision screws with the piston displacements being sensed by counting the drive screw rotational increments. These increments are produced electrically by sensing the resistance changes produced in a photoresistor as a chopping device attached to the drive screw interrupts a light beam. These chopping devices divide one screw revolution into one hundred increments by interrupting a light beam. The pulses from these devices are suitably conditioned by comparators, then counted by an electronic counter. This counter may be preset to any number up to 9999 with different presets for each unit. In the delivery mode, power to the screw drive motor is shut off and delivery stops upon counting down to 0000.

The unit must be connected to a reservoir and the drive motor reversed in order to refill the device. A motor driven valve is used to make this connection. The valve positioning and the syringe motor operation is controlled by a solid state sequencing device. This sequencing device prevents the valve motor and the screw drive motor from both running at the same time.

The system consists of the syringe units shown (Figures 1 and 2) and the associated counting and control circuitry. Provision has been built into the electronics for a third syringe. Syringe one (Figure 1) is based on the previously mentioned extensively modified commercial unit. Syringe two (Figure 2), as well as the counting and control
1. Chopper disc
2. Lamp
3. Photoresistor
4. Motor
5. Piston
6. Carriage
7. Syringe body
8. Drive screw
9. Valve motor
10. Position switches
11. Valve
12. Ball joint
13. Refill switch

Figure 1
Drawing of Syringe 1
1. Chopper disc
2. Lamp
3. Photoresistor
4. Motor
5. Piston
6. Carriage
7. Syringe body
8. Drive screw
9. Valve motor
10. Position switches
11. Valve
12. Ball joint
13. Refill switch

Figure 2

Drawing of Syringe 2
circuitry, has been designed and constructed during this work. The
counting and control circuitry is housed in an aluminum chassis.

**Integrated Circuit Electronics**

Electronics has become to a large extent a field of package
selection and utilization. It is not usually necessary to know how
an integrated circuit treats an electrical signal internally so long
as its input/output characteristics are clearly understood. Several
types of integrated circuit digital electronic packages are available.
The type employed in this system belongs to the family known as
transistor-transistor logic, TTL. TTL employs transistors as on-off
switches in a multitude of circuit types. All of these types have
as their basis the gate concept. A gate may be thought of as an
electronic circuit which is acted on by a signal and caused to open
or close. It is useful to understand the operation of the two basic
TTL gates, the "NAND" gate and the "NOR" gate in order to understand
the concept of current sinking logic as well as the concept of package
circuitry. These two concepts are essential for work involving TTL
devices.

Two concepts must be presented before the examination of these
gates. The accepted nomenclature of digital electronic devices allows
a positive signal (+5 volts d. c.) to be referred to as a "high state"
or "high." Similarly, a ground potential (0 volts d. c.) is referred
to as a "low state" or a "low." The second concept needed is that of
the truth table. A truth table compactly represents the input to
output relationships of digital electronic devices. Each input is
equivalent when designated by the same letter type. Thus a device
with three equivalent inputs may have all possible input combinations
described by only four combinations. In truth tables, a high state
is represented by a 1 and a low state by a 0. These are also referred to as the logic levels of the truth table.

The "NAND" gate may be used to demonstrate the operation of TTL gates.² The schematic symbol and truth table for a NAND gate are given in Figure 3.

![NAND Schematic Symbol and Truth Table](image.png)

**Figure 3**

NAND Schematic Symbol and Truth Table

As seen from the truth table, the output is high only if all inputs are not high. The output is low if all inputs are high. An output in the low state "sinks" current (diverts current to ground) furnished to it. Thus TTL gates are said to involve current sinking logic. The name of this gate becomes obvious if the truth table is interpreted as meaning not A and B (and C) or "NAND." This means the output will be "true" (=1) only when all of A and B and C are not "true."

The "NOR" gate, similarly is not A or B.³ The truth table and schematic symbol for this device are shown in Figure 4. As may be seen from the truth table, this device only gives a high output in response to all of its inputs being held high. If any input is held low, the output is low. If A or B is "true" (=1), the output is 1. The output, however, is "not" A or B, therefore it is 0.
A third type of unit essential to digital electronics and based on the "NOR" and "NAND" gate concepts is the "Flip-flop." As the name implies, this is a bistable device. Its output may be forced into the high or the low state by proper inputs. Once the output reaches one of these states, it will remain in that state until another input forces a change. This type of device consists of several suitably connected "NAND" and "NOR" gates enclosed in a single package. It is possible to understand the action of such a device by direct circuit analysis or by the use of the "NAND" and "NOR" gate concepts previously discussed. Such an analysis is not necessary to understand the action of this device. By making use of the same type of package analysis by means of the truth table as was employed in the discussion of the "NAND" and "NOR" gates, the action of this device may be easily understood. Figure 5 gives the schematic symbol and the truth table for a typical "flip-flop."

The device outputs are designated Q and \( \overline{Q} \). As the notation implies, Q is the opposite of \( \overline{Q} \). Since 1 is the opposite of 0 in digital electronics, if Q is 1, then \( \overline{Q} \) must be 0. If Q is 0, the \( \overline{Q} \) output must be 1. Ignoring for the moment the other inputs, the \( T \) input action
Figure 5
Flip-flop Schematic Symbol and Truth Table

may be examined. If T is raised from the low state to the high state, then returned to the low state, the device has been "toggled."
Toggling causes the Q and \( \overline{Q} \) outputs to change state. If Q was in the high state before toggling, it will be in the low state after toggling. Similarly, if \( \overline{Q} \) was in the high state before toggling, it will be in the low state after toggling. If the device is repeatedly toggled, the outputs will be in their initial state after every second toggle. This merely divides the toggle frequency by two as shown in Figure 6.

Figure 6
Flip-flop Behavior During Toggling
If several flip-flops are cascaded (each T input is connected to the Q output of the preceding unit), a binary counter has been constructed. The first flip-flop would divide the input frequency by \(2^1\), the second by \(2^2\), and the nth by \(2^n\).

The other inputs for the flip-flop are the J, K, set, and clear inputs. The set and clear inputs may be used to preset the output state of the device. If the set input is taken from a high state to a low state, then returned to the high state, the output Q is set to the high state. Similarly, if the clear input is taken from a high state to a low state, then returned to the high state, the output Q is cleared to the low state. The J and K inputs may be thought of as inhibit inputs since they inhibit specific changes in the output when activated. If any J is held low, Q will not change from the low state to the high state when the device is toggled. If any K is held low, Q will not change from the high state to the low state when the device is toggled. This is shown in the device truth table (Figure 5). The heading \(t_n\) denotes the state of the particular input or output at toggle impulse n. The heading \(t_{n+1}\) denotes the state of the particular input or output at toggle impulse \(n+1\), the next impulse. It may be seen that if both J and K are low, no change in Q takes place upon toggling. If both J and K are high, normal toggling takes place.

From the preceding, it is obvious that such devices are capable of handling binary information. Since numbers are more easily worked with in decimal form by most people, electronics manufacturers have provided digital electronic devices which accept decimal information. The devices still operate in a binary system, but their inputs and outputs allow users to easily convert to decimal.
One popular approach to this is to use binary coded decimal which is usually denoted as BCD.\textsuperscript{5} Binary coded decimal is a means of easily converting decimal numbers to easily understood binary numbers. The binary coded decimal systems assign each of the binary positions a value such that four binary digits represent one decimal digit. The 8-4-2-1 binary coded decimal system assigns the fourth position to eights, the third to fours, the second to twos, and the first to ones. This is identical to binary. The fifth through the eighth positions, however, repeat this assignment for the second digit of the decimal number being converted. Each decimal digit is represented by a group of four binary digits. A number such as 2719 would be represented in the following manner in 8-4-2-1 binary coded decimal.

<table>
<thead>
<tr>
<th>Decimal digit</th>
<th>8-4-2-1 Coded form</th>
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<tr>
<td>2</td>
<td>0010</td>
</tr>
<tr>
<td>7</td>
<td>0111</td>
</tr>
<tr>
<td>1</td>
<td>0001</td>
</tr>
<tr>
<td>9</td>
<td>1001</td>
</tr>
</tbody>
</table>

2719 = 0010011100011001

This coding method allows immediate recognition of the decimal number equivalent for any such binary coded number. By comparison, the true binary form of 2719, 101010011111, is much more difficult to recognize.

It is possible to connect devices such as the "Flip-flop" in such a way that a series of these devices is capable of decimal counting even though their actual operation must be binary. It is common practice to incorporate the circuitry needed for this in a single package. Such packages are commonly called decimal counters or simply counters. These packages can be furnished with large amounts of
auxiliary circuitry for special applications such as detection of a specific number of counts. Packaged circuits are currently available which contain all elements for a multidigit decade counter, count display, and memory in a single unit.

The circuits described are basic units of TTL circuitry and are found in some form in almost all TTL packages. These packages are known as integrated circuits (IC's). These are small plastic or ceramic capsules which house the semiconductor chip which contains the circuit components needed for these devices. These are encapsulated for the purposes of electrical insulation, mechanical protection, compactness, and ease of replacement. Each such package is described by the operating parameters and characteristics furnished by the manufacturer. This information enables a unique electronic approach in that circuit design does not depend on intimate knowledge of the actual circuitry of the device, but rather on what its operational capabilities and requirements are.

The principle benefit from the use of IC packaged electronic devices is that of drastically reduced cost. A simple NAND gate would require five transistors and several resistors to duplicate using discrete components. This would cost approximately ten times what the commercially available IC costs. A simple flip-flop employs on the order of eight such gates at a cost perhaps one percent of the cost of an equivalent assembly using discrete components.

Integrated circuits are highly reliable and have long life expectancy. Although electronics manufacturers admit that solid state devices fail after long use, reliability data is normally stated in terms of average lifetime at high overloads. These may be interpreted as giving continuous use lifetimes on the order of tens of years without failure.
Subunit Descriptions

The sampling system is divided into several subunits as shown in Figure 7. Each of these may be described as a separate unit with respect to description, functional explanation, and construction details. Information for electrical interconnections between subunits is contained in the Appendix as well as the specific component values for the subunits.

**Photoresistor Comparator**

The photoresistor comparator consists of a photoresistor and a solid state comparator. A light beam is interrupted by a chopper before falling on the photoresistor. The chopping device is a four inch aluminum disc with one hundred evenly spaced holes around its periphery. Light falling upon the photoresistor through one of these holes causes a drop in resistance of this component. The chopping disc is rigidly attached to the drive screw. Any rotation of the drive screw alternately illuminates and darkens the photoresistor. The resultant oscillating waveform is conditioned by the comparator for compatibility with the counter circuitry as shown in Figure 8. The light source is a common incandescent bulb of the type used by many commercially available flashlights.

As may be seen from the circuit diagram, Figure 9, the comparator is a triple unit capable of accepting chosen inputs from any of three independent sources and giving an output to a single terminal. The comparator subunit is constructed on a circuit board which may be individually removed from the main electronics chassis for inspection. The output of the comparators is directly TTL compatible and of very low noise characteristics.

The comparators themselves are LM311H units by Fairchild Electronics.\(^6\) This type of device gives a high output if no difference
Figure 7
Block Diagram of the Sampling System
Figure 8
Illustration of Photoresistor Output and Comparator Output
Figure 9
Circuit Diagram of the Comparator
is detected between two input voltages. The output is in the low state if a difference is detected. External circuitry determines the sign and magnitude of difference necessary for the output to be in the low state. The external circuitry enables the operator to set a high and low trigger threshold to achieve the best counting behavior by means of potentiometer 1,3,5 and 2,4,6, respectively. This circuit interacts with the strobe circuit, the photocell circuit, and the counter. Connections S1, S2, and S3 are the strobe inputs. If S1, S2, or S3 is high, then IC1, IC2, or IC3 output is high. These inputs, S1, S2, and S3, are connected to the corresponding outputs of the comparator strobe control. I1, I2, and I3 are the photoresistor inputs which are connected to the photoresistors of units 1, 2, and 3. Potentiometers P1, P3, and P5 set the voltage across the photocell. Potentiometers P2, P4, and P6 set the trigger level of the comparator. Capacitors C1, C2, and C3 assist in increasing the noise immunity of the unit.

**Counter Encoder**

The counter consists of four cascaded binary coded decimal presettable up/down counters, Texas Instruments SN74192N. The device outline and parameters are shown in Figure 10. These devices operate in the 8-4-2-1 BCD mode and have data outputs which furnish a continuous readout of the counters' internal states. In operation, the counter is preset by momentarily grounding the load input while presenting the desired preset at the data input terminals. This sets the starting point into the counter. If the count down input is held high and the count up input is toggled as shown in Figure 10, the counter will count up. The counter counts up to zero from 7, pulses the borrow output and continues. If the count up input is held high and the
$V_{cc}$ - supply voltage = 5 volts d.c. at 65 mA.
Count frequency = 25 MHz. maximum.

Device Behavior During Operation

Count State Outputs
- \( Q_A \)
- \( Q_B \)
- \( Q_C \)
- \( Q_D \)

Count State in Decimal: 0 7 8 9 0 1 2 1 0 9 8 7

Figure 10
Decade Counter, Operating Parameters and Behavior During Counting
count down input pulsed, the counter counts down in the same manner. The clear input overrides all counter functions and sets the counter to zero when pulsed high. The output from the comparator is applied to one count input while the other count input is held high. The counter output goes low momentarily upon zero crossing to trigger the next stage.

Figure 11 shows the overall wiring diagram for the four-decade counter constructed from these units. The A, B, C, and D inputs are the preset inputs. They are connected to encoding devices which convert decimal to binary coded decimal in 8-4-2-1 code. The load and clear inputs are paralleled as shown. Each counter drives the next by way of the borrow and carry outputs operating upon the count up and count down inputs of the next stage. The final stage carry output drives the sequencer by way of the counter sequencer interface. The first stage is driven by the comparator. The count direction switch connects the comparator to the desired counter input while holding the other input high.

The counter is loaded by the use of decimal to 8-4-2-1 BCD encoders. These encoders are rotary thumbwheel switches which display a decimal number while making proper connections for the encoded for that number. The wiring diagram is shown in Figure 12. This is a rear view of the encoder bank. Each encoder bank corresponds to a preset for a particular delivery unit. The encoder bank needed is selected by the master sequencer and pulsed when directed along with the counter load input. This gives a high input to the needed counter inputs (ABCD Preset Inputs of Figure 10) to achieve the desired presets. The diode matrix prevents any signal but that from the selected encoder bank from reaching the counter inputs. The power supply to the counter is decoupled by a capacitor to
Figure 11
Circuit Diagram of the Counter
Figure 12

Circuit Diagram of the Encoder
minimize transients in the power supply and conventional wiring techniques. The diode matrix is constructed on the plug connectors of the encoders and consists of ordinary 1N914 diodes.

**Decoder Driver Display**

The display is made up of four Monsanto MAN4A seven segment light emitting diode (LED) integrated circuits. Figure 13 gives the device outline and the appearance of the readout for the decimal numbers as well as the device parameters. The circuit diagram for the display is given in Figure 14.

Since the counter output is in 8-4-2-1 BCD, this must be converted to suitable seven segment code for the display. This is the function of the Monsanto SD101 decoder/drivers whose device outline, operating parameters, and truth table are shown in Figure 15. The wiring diagram for these units is shown in Figure 16. These units function not only as encoding converters, but as driver units to furnish sufficient power for the display.

**Sequencer Valve Switching Network**

This unit is the motor power control unit (Figure 17). Line current is switched by the silicon controlled rectifier hookup shown. When the rectifier gates are connected to each other, the rectifier pairs conduct line current. This connection is made by way of reed relays as shown in the circuit diagram. The three rectifier pairs control the motors in the delivery, refill, and valve positioning modes. Voltage applied to terminal 1 closes R1 causing SCR3-SCR4 to conduct line current to the valve motor until the valve delivery position microswitch opens. This interrupts current to R1 and shuts down the valve motor. This microswitch, when open, directs power to terminal 3. This closes R4 which causes SCR7-SCR8 to conduct and run the delivery
Cont. forward current 15 mA/segment max.
Forward voltage 1.7 @ mA/segment typ.
Brightness 200 ft-L @ 5 mA
Peak emission 6300-7000 A

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<tr>
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</tr>
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<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>ABDFG</td>
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<td>ABCDEF</td>
</tr>
</tbody>
</table>

Figure 13
Counter Display Outline, Operating Parameters, and Display Appearance for the Decimal Numbers
Figure 14

Circuit Diagram of the Display
The blanking input/ripple blanking output (BI/RBO) is held high at all times in this application.
The ripple blanking input (RBI) is also always held high.
The lamp test input (LT) is not used—left unconnected.

\[ V_{cc} \text{— power at 5 volts d.c. at 40 mA} \]

**Figure 15**

Decoder/Driver, Operating Parameters, and Truth Table
Figure 17

Circuit Diagram of the Sequencer
motor forward until power is removed by the counter by way of the counter sequencer interface upon delivery completion. A pulse at connector 4 initiates the refill sequence by turning on SCR1 and SCR2. SCR2 receives current through relay R3 which is supplied through a 32K\ohm resistor. This is enough current to hold SCR2 on while not enough to actuate relay R3. SCR1, however, turns on relay R2. This turns on SCR3-SCR4 to supply line current to the valve motor until the refill microswitch is actuated. This actuation removes current from relay R2 and directs this current to R3, thereby turning off SCR1. Actuating R3 causes SCR5-SCR6 to apply line current to the refill windings of the syringe motor until the rear limit switch is contacted, breaking the circuit to R3 and shutting off SCR2. Opening this switch applies voltage to R4. This causes SCR7-SCR8 to conduct, running the delivery motor until the switch again closes. Action then halts until another command is received. Operation commands for this unit come from the sequencer interval timer and from the counter sequencer interface. The microswitches are located as shown in Figure 18 and actuated by the arms of the valve and by the piston carriage. Figure 18 also shows the overall wiring scheme for the syringe units.

**Counter Sequencer Interface**

This subunit (Figure 19) consists of a JK flip-flop connected as a latching device. This subunit functions to interface between the counter which operates at five volts and the sequencer which operates at higher voltage. This operates a reed relay by way of a transistor. This in turn supplies current to terminal 1 of the sequencer to perform the delivery operation. The circuit is triggered into the on (relay actuated) state by a pulse from the master sequencer. The circuit is shut off (relay opened) state by a pulse from the counter borrow
1* Common Refill Switch (brown)
2  Normally Open Refill Switch (green)
3  Common Delivery Switch (blue)
4  Normally Open Refill Switch (orange)
5  Normally Closed Limit Switch (white #3)
6  Photoresistor (white)
7  Photoresistor (white)
8  Common Limit Switch (white #1)
9  Normally Open Limit Switch (white #2)

Stopcock Motor

Drive Motor

10 Drive Motor Common (black)
11 Drive Motor Deliver (gray)
12 Drive Motor Refill (yellow)
13 Power Stopcock Motor (black)
14 Power Stopcock Motor (black)
15 Chopper Bulb (white/yellow)
16 Chopper Bulb (white/yellow)
17 Normally Closed Delivery Switch (purple/white)
18 Normally Closed Refill Switch (purple)

Figure 18
Syringe Wiring Diagram
Figure 19. Circuit Diagram of the Counter Sequencer Interface
output. The turn on command from the master sequencer also activates the load function of the counter and supplies the necessary encoder with power. The circuit diagram also shows the "clear" push button switch which halts delivery if depressed momentarily. This subunit is connected as shown to the counter borrow output (CLK), the "load" command line (L), and to the sequencer (S). A capacitor is used to bypass any noise in the "load" circuit to ground to prevent spurious triggering and subsequent malfunction.

**Master Sequencer**

The master sequencer originates the sequential commands necessary for automatic operation of the system and institutes these commands. The major circuit involved in this subunit is the unijunction transistor (UJT) timing circuit. Figure 20 shows a simple UJT timing circuit. The capacitor charges through the variable resistor until the firing voltage of the UJT is reached, then the UJT turns on and the unit conducts. This discharges the capacitor and produces a sharp voltage drop at 1 and a sharp spike at 2. The time interval depends on the values of the variable resistor and the capacitor.

Figure 21 gives the circuit diagram of the master sequencer. This unit employs, for each syringe, a "flip-flop," a unijunction transistor, two conventional transistors, and a few essential resistors. In operation, grounding P grounds the preset input of the flip-flop to raise Q to a high state and start the UJT timer circuit. When the UJT fires, the generated pulse grounds "clear" and L to return the "flip-flop" Q to the low state and thereby turning off the timer. The grounding of L presets the counter sequencer interface. Transistor Q1 is also connected to the strobe control in a manner to be explained later. When the UJT fires, it also triggers the sequencer of the
Figure 20

Typical Unijunction Transistor Timing Circuit
Figure 21. Circuit Diagram of the Master Sequencer
previously delivered syringe to refill. By properly wiring the three switches, the strobe controls, the counter sequencer interface, the sequencers, and the panel control buttons, the correct automatic sequence of operations is accomplished with enough delay time between deliveries to enable facile reading of the display.

Comparator Strobe Control

The comparator strobe control subunit (Figure 22) functions to turn off the two unused comparators while allowing the selected unit to produce input for the counter. If either the sequencer interval timer or the counter sequencer interface is in the high state, the comparator will be on. If both these inputs are low, the output of this unit to the comparator is in the high state holding the comparator out high by way of the comparator strobe input. The inputs are guarded by diodes to prevent cross interactions between the master sequencer timer and the counter sequencer interface. The overall function, then, is if the unit is running or in the timed interval immediately following running, the comparator is turned on. This allows all deliberate counts and all over-run counts to be counted.

Power Supply

As may be seen from the circuit diagrams previously given, TTL power at 5 volts d.c., relay-sequencer power at 12 volts d.c. and lamp power at 3 volts d.c. are required. The 5 volts d.c. must be well regulated as must the 3 volts d.c. The 12 volts d.c. need only be well filtered. The diagram of Figure 23 shows the power supply. The 3 volts d.c. and 5 volts d.c. come from the regulated section. The regulator circuit is a series pass power transistor controlled by a Fairchild μA723 solid state regulator. The power is furnished by a 12.6 volts transformer and a full wave bridge rectifier. Filtering is
Figure 22
Circuit Diagram of the Comparator Strobe Control
1, 2 - 110 volts a.c.
3 - 12 volts d.c.
4 - 5 volts d.c. ± .2 volts variable by the potentiometer
     ripple less than 2 mV under full load

Figure 23

Circuit Diagram of the Power Supply
accomplished by a large electrolytic capacitor. The voltage is stepped down by a power resistor to lower the voltage drop and hence the power dissipation at the series pass transistor. The integrated circuit gives active regulation by means of an internal zener diode driving an error amplifier. This amplifier detects the difference between the zener reference voltage and the voltage at the output. This signal is then amplified and used to drive the external transistor to regulate the output voltage at 5 volts d.c. The 12 volt d.c. power and 3 volt d.c. power are tapped from the power supply as shown. The power supply is constructed on a small sub-chassis which may be removed from the main chassis by the removal of four attaching screws and the two electrical plugs.

**Chassis Design**

The main chassis was constructed of one-eighth inch aluminum. Each subunit is attached to the main chassis by screws and make use of electrical plugs to facilitate servicing. The front panel swings forward to expose all internal components. The sequencers, power supply, and main terminal strips are attached to the main chassis. All other sub-units and control switches are mounted on the front panel. Figure 24 shows the internal subunit layout and front panel layout of the main chassis. Connection to each syringe unit is by multiconductor cable of the code indicated on the syringe wiring diagram. The chassis fuses, the power supply power transistor, chassis cooling fan, and voltage dropping resistor are mounted on the back of the chassis.

**Pump Construction**

Syringe unit 1 was the previously mentioned commercially available unit which was modified to resemble syringe unit 2. Syringe unit 2 was constructed during this work in the following manner. The syringe
1. Power Supply
2. Sequencers
3. Master Sequencer
4. Counter Sequencer Interface
5. LED Display
6. Counter/Decoder
7. Encoder 3
8. Encoder 2
9. Encoder 1
10. Comparators
11. Comparator Strobe
12. Mode Switch
13. Count Direction Switch
14. Motor Indicator Lights
15. Start 3/Refill 2
16. Start 2/Refill 1
17. Start 1/Refill 3
18. Power Switch
19. Titrate/Normal Switch
20. Titrate/Deliver Button
21. Power Indicator Lamp
22. Power Line
23. Unit 1 Cable (red)
24. Unit 2 Cable (red)
25. Unit 1 Cable (green)
26. Unit 2 Cable (green)
27. Blower
28. Power Supply Transistor
29. Power Resistor Connection
30. Power Resistor Connection
31. 13 Tab Terminal Strip
32. 13 Tab Terminal Strip
33. 26 Tab Terminal Strip
34. Fuse

Figure 24. Drawing of Main Chassis with Internal Subunit Positions
chassis was of aluminum construction but did employ steel carriage
guide rods. The piston was machined from stainless steel to a diameter
of 0.751 inch, then polished using silicon carbide abrasive to achieve
an exact 0.7500 inch diameter and exceedingly smooth finish. Piston
carriage detail is shown in Figure 25 as is the piston seal flange.
This piece was machined of mild steel with O-rings being used to accom-
plish sealing. The glass portion of the syringe is shown in Figure 26.
This figure also shows the three way valve assembly. The valve is a
conventional three position stopcock with Teflon plug. This valve was
placed in a roughly machined aluminum collar and fixed in place with
epoxy cement. The aluminum collar allowed it to be rigidly attached
to the chassis. The chopper disc is a four inch aluminum disc with
one hundred equally spaced holes bored around its edge as shown in
Figure 27. The photocell and lamp holder was machined from aluminum
blocks as shown in Figure 28. The delivery tips were constructed of
capillary tubing with drawn out tips as shown in Figure 29. They are
of sloping design to prevent trapping of bubbles in unavoidable enlarge-
ments in the tubing during initial loading of the system with solution.
The reservoirs are of the design shown in Figure 30. This design allows
the reservoirs to be easily hooked to the syringes while also allowing
the reagents they contain to be kept under an atmosphere of inert gas.

Cell Holder

A thermostatted cell holder was constructed as shown in Figure 31
in order to easily use the sampling system in conjunction with a
Cary 14 spectrophotometer. A stirring magnet mounted in the base of
the brass block gives a means of stirring a solution in a cell placed
in the block. This magnet is driven by an O-ring from a shaft turned
by an external motor. A conventional 1 cm. rectangular cell is used
Piston Carriage

Seal Flange

Figure 25

Drawing of the Piston Carriage and the Piston Seal Flange
Figure 26

Drawing of the Glass Syringe Body and the Valve Assembly
Figure 27

Drawing of the Chopper Disc
Figure 28

Drawing of the Photoresistor-Lamp Holder
Figure 29

Drawing of the Delivery Tips
Figure 30

Drawing of the Liquid Reservoirs
Internal Coolant Passages

Stirring Magnet Pulley
- Magnet Mounted on Concealed End of Shaft

Figure 31
Drawing of the Thermostatted Cell Holder/Stirrer
in the cell block. An all glass solenoid valve (Figure 32) functions to empty the cell by applying aspirator vacuum to a capillary tube extending to the bottom of the cell. The tips, a gas tube, the capillary emptying tube, and a thermistor are held in position by a Teflon cap as shown in Figure 33. All interconnections involving glass pieces are made using high vacuum O-ring ball joints.

**Modifications**

Several modifications would greatly enhance this system. By placing the glass portion and piston in a vertical configuration, initial loading of the syringe would be much easier. Using a collinear piston, screw, motor arrangement would minimize inaccuracies arising from wear. The use of a stepper motor and variable oscillator in conjunction with the same type of counter employed in the present design would improve delivery accuracy by enabling the unit to slow delivery speed as the endpoint is reached as well as eliminating the light chopper itself. By using a commercially available rotation encoder capable of producing many pulses per revolution, the chopper could be eliminated along with the lamp and photoresistor. Alternatively, the same disc approach and a light emitting diode as the light source would greatly decrease servicing frequency. The counter may now be purchased in the form of monolithic counter-decoder-driver-latch-display units. This would decrease the number of components by eight which should give considerably better lifetime of service. The system would be more flexible if the subunits were made capable of independent operation for other purposes; an events counter, for example. The use of microswitches for valve positioning and refill position sensing should be eliminated by replacing them with solid state light sensing devices. The system should be equipped with a printer capability to permanently record
Figure 32
Drawing of the Glass Solenoid Valve
Tips and emptying tube extend to bottom of cell. Thermistor extends to 1 cm. from top of cell.

**Figure 33**

Drawing of the Cell Cap Showing Positions of the Tips, Emptying Tube, and Magnetic Stirring Bar
deliveries. Some type of input device such as a card or punched paper tape reader would also prove to be of great use. The encoders were chosen for the reason that this conversion would be easily accomplished since all operations are electrical in the present device.

In the event that it is desired to employ this system in the handling solutions that are sensitive to the materials used in the piston, seals, or seal holder, it is possible to avoid contact between the liquid being handled and these parts. If the syringe body is filled part way with mercury, these parts will not be contacted by the liquid being handled while the system is in use.
Operation

Initial Hookup

The main supply should be 110-120 volts a.c. using a grounded receptacle for safety. Each syringe unit is connected to the main chassis by a green and a red multiconductor cable. These cables are permanently attached to the main chassis and are merely plugged into the syringe unit receptacles. Alignment of all motors with their driven shafts is checked visually, particularly the valve motors and adjusted if misaligned. The front panel detail in Figure 34 gives the appearance of the front panel controls and indicator lights as well as the control switches. Upon turning on the master power switch, the main pilot lamp should light. No other indicator lights should be on at this time except, of course, the display. The display will show an indeterminate set of figures depending on the initial state achieved by the counter upon application of power.

Front Panel Controls

The main power switch controls line power to the entire unit with the pilot lamps indicating any motors which are running. The mode switch, when in the auto position, causes syringe two to begin delivery after syringe one has completed its delivery. If this switch is in the man. position, each syringe delivery must be actuated manually. The deliver switch initiates delivery for the syringe named when it is momentarily depressed. When the mode switch is in the manual position, however, this same momentary depression of the deliver switch only refills the immediately preceding unit. The clear pushbutton sets the count to zero. This halts delivery immediately by way of an artificial zero-crossing of the counter. The titrate switch turns on comparator one for use in manual delivery. The titrate pushbutton,
Figure 34

Drawing of the Front Panel
when held depressed, positions the valve to the delivery position, then delivers from unit one until released. During this delivery, it is possible to display directly the counts of solution delivered by placing the count dir. switch in the count up position. This causes the counter to count up from zero, giving a direct display. The aliquot switch, located at the valve of unit one, causes this unit to refill from the tip rather than from the reservoir. This allows the operation to withdraw a measured aliquot of sample, then deliver it.

**Delivery Mode**

In order to automatically deliver unit one, unit two, and refill each, the following switch positions are used:

- **Mode - Auto.**
- **Count Dir. - Down**
- **Titrater - Off**
- **Preset - (desired delivery volume)**

To initiate delivery the deliver one switch is depressed and released. After a delay of ten seconds, the unit one encoder setting is loaded into the counter and displayed. The valve motor indicator light will not be on indicating that the unit one valve is being positioned to deliver. When the valve reaches this position, the valve motor shuts off. The delivery motor then starts to deliver the preset volume. The counter will then count down to zero as delivery is made, the motor will shut off, and the motor coast will be displayed as 0000-overrun. After a ten second delay, unit two begins its delivery sequence. At this time unit one will reposition its valve to the refill position, then reverse the delivery motor until the rear refill switch is opened. This causes the motor to run forward until the rear refill switch again closes. Thus the system removes all back lash in the gear drive to improve its precision and accuracy. Unit two will meanwhile deliver, display overrun, then refill.
Manual Mode

In the manual mode, all conditions are the same except for setting the mode switch to manual. Depressing the deliver one switch will now cause unit one to load, deliver, and refill. Action will then cease until further commands are furnished. To initiate delivery of unit two, deliver two is momentarily depressed. This feature allows the operator to deliver from unit two before delivering from unit one if this is desired.

Titrate Mode

The titrate mode allows manual addition of volumes of reagent by use of the following settings:

Mode - Man.  Count Dir. - Up
           Titrate - On  Clear - (depress to clear counter)

Depressing the titrate pushbutton positions the valve to deliver and runs the delivery motor until the button is released. The volume delivered is displayed directly.

Aliquot Mode

The aliquot mode is identical to the titrate mode except for the source of reagent. First an amount in excess of the desired aliquot is delivered. The aliquot switch is immediately depressed and held depressed. This causes the syringe to refill from the tip rather than the reservoir, drawing in an aliquot of any liquid placed at the tip. Then a normal delivery will deliver the aliquot from the tip.
CALIBRATION

In order to calibrate the two syringes, water was delivered into tared containers, weighed, and the counts per gram calculated. This data is displayed along with its standard deviation in Tables 1 and 2. Use of the delivery, titrate, and aliquot modes gave no different results, indicating that all of the automatic sections operate normally. Screw linearity was checked by starting a delivery after the delivery of 1000 counts without allowing the unit to refill. No difference in calibration was observed indicating good piston precision and screw linearity.

A spectrophotometric calibration was done using a solution of well known absorption characteristics. An aqueous solution containing 0.0350 gm potassium chromate and 2.00 gm of potassium hydroxide per liter of water at 23°C has an absorption maximum at 373 nm of 0.870 absorbance units. This solution was placed in the reservoir of unit two. After placing water in the unit one reservoir, the system was used to prepare a series of samples of various concentrations. The absorbance of these solutions was measured using a Cary 14 recording spectrophotometer. A Beer's law plot of the data so obtained is shown in Figure 35. The linearity of the plot demonstrates graphically the delivery precision of the system. The $E_1^1$ obtained from the slope of the line in Figure 35 is 248.9 (lit. $E_1^1 = 248.5 \pm 1$).

Sources of Error

There is an inherent maximum error of two counts in each unit due to the incremental nature of the counting method used. The largest error contributor other than the increment error is due to temperature variations. Dimensional changes in the tips have been minimized by the use of glass capillary tubing, but the metal portions of each unit
(the carriage, the piston, and the screw) can produce errors if the ambient temperature fluctuates. Dimensional changes in the glass syringe body will, of course, have the same effect. Such temperature fluctuation effects were minimized by the use of an external thermostatted bath circulating coolant through flexible heat exchange tubing wrapped around each syringe. The final major source of error is mechanical wear. This has been minimized to some extent by the backlash removal feature. Such wear would require the replacement of the drive screw after a long period of use but such wear has not been detected during this work.
<table>
<thead>
<tr>
<th>Grams Delivered</th>
<th>Deviation</th>
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<td>5.4105</td>
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<td>.0012</td>
</tr>
<tr>
<td>5.4228</td>
<td>.0053</td>
</tr>
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</table>

\[
5.4175 = \text{average} \quad \text{standard deviation} = .00722
\]

Large syringe preset at 1500 counts. Weight of water delivered used to calibrate the syringe.

\[
\frac{5.4175 \text{ grams}}{1500 \text{ counts}} = 3.61167 \times 10^{-3} \text{ grams/count}
\]

\[
\frac{.00722 \text{ grams}}{1500 \text{ counts}} = 4.8133 \times 10^{-6} \text{ grams/count st. dev.}
\]

Overall Calibration gives \( .0036117 \pm .0000048 \text{ gm/count} \)

\[
\frac{.0036117 \text{ gm/count}}{.99780 \text{ gm/ml at } 22^\circ \text{C}} = .0036197 \text{ ml/count at } 22^\circ \text{C}
\]

**Table 1**

Typical Data from the Syringe 1 Calibration
Small Syringe Preset to Deliver 4000 Counts Water at 23°C.

Grams Water Delivered

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<tr>
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<tr>
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<td>8.770</td>
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<td>1.070</td>
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<td>3.9959</td>
<td>9.670</td>
</tr>
<tr>
<td>3.9678</td>
<td>-18.43</td>
</tr>
</tbody>
</table>

3.9862 ave.

Standard Deviation = 0.02073

$.00099666 \text{ gm/count} + .99780 \text{ gm/ml at 22°C} =$

Volume/count in liters = $.0009988 \text{ ml/count at 22°C}$

Table 2

Typical Data from the Syringe 2 Calibration
slope = $4.0184 \times 10^{-3}$

$E_1^1 = 1 / \text{slope} = 248.9$

Figure 35

The Absorbance Versus %Chromate Calibration Plot
References

1. J. Bartmess, undergraduate research report presented to Prof. E. S. Lewis, Rice University, May 14, 1970.


4. Ref. 3, p. 6-3.


9. Ref. 8, p. 35.


PART II

TRIPHENYLMETHYL: DISSOCIATION EQUILIBRIUM
AND REACTION WITH THIOPHENOL
Introduction

In 1900, Gomberg attempted to prepare the fully phenylated ethane as the next logical step after his preparation of tetraphenylmethane. His initial attempt at this synthesis was the treatment of triphenylmethyl bromide with sodium. This reaction proved unsatisfactory, so the reaction was attempted using finely divided silver ("molecular" silver) and triphenylmethylbromide. A white solid was isolated, but the elemental analysis indicated it was not a hydrocarbon but in fact contained oxygen. This material was identified as triphenylmethylperoxide. The oxygen incorporated in the product molecule therefore had to come either from the silver itself in the form of an impurity, or from oxygen dissolved in the reaction solution. Subsequent experiments with scrupulously purified silver as well as with mercury and zinc gave the identical product. This led to the conclusion that the incorporated oxygen came from oxygen dissolved in the reaction mixture. By attempting the synthesis under an atmosphere of carbon dioxide, Gomberg succeeded in producing a yellow colored solution. By carefully excluding oxygen, a white solid could be isolated. This white solid produced a yellow solution in organic solvents in the absence of air. These yellow solutions again gave triphenylmethyl peroxide upon exposure to air. The white solid was originally thought to be the triphenylmethyl radical.

Molecular weight determinations of Gomberg's compound gave unexpected results.² If solutions of the compound contained only triphenylmethyl, the molecular weight should be 243. The experimentally determined molecular weight was much higher than this, but not
high enough to be hexaphenylethane at 486. Although the data were not consistent, the observed molecular weights always fell between these two values.

In 1904, Gomberg and Cone proposed that an equilibrium was being observed in solutions of the compound\(^2a\)

\[
\text{Ph}_3\text{CCPh}_3 \rightleftharpoons \text{Ph}_3\text{C}^+ + \text{Ph}_3\text{C}^- \quad (1)
\]

This would give molecular weight values between the molecular weights of the two materials and explain the observed phenomena.

Further evidence for the equilibrium came from the behavior of solutions of the solid with air. If a solution is prepared of this solid, it is yellow. Upon exposure to air, the solution becomes clear and a white solid precipitates. If air is the removed, the solution again becomes yellow. The solid which precipitates is triphenylmethyl peroxide. This procedure may be repeated until all of the original substance has been consumed.

It would be expected that measuring the rate of the reaction with oxygen would give a measure of the rate of the dissociation. The rate of reaction with oxygen, however, proves to be much faster than the reaction with nitric oxide which might be expected to be the same type of reaction\(^3,4,5\). This led to the conclusion that oxygen reacts by a different mechanism. This has been formulated as shown in Scheme 1.

SCHEME 1

\[
\text{Ph}_3\text{CCPh}_3 \rightleftharpoons \text{Ph}_3\text{C}^+ + \text{Ph}_3\text{C}^- \quad (2)
\]
\[
\text{Ph}_3\text{C}^+ + \text{O}_2 \rightleftharpoons \text{Ph}_3\text{COO}^- \quad (3)
\]
\[
\text{Ph}_3\text{COO}^- + \text{Ph}_3\text{C}^- \rightleftharpoons \text{Ph}_3\text{COOCPh}_3 \quad (4)
\]
\[ \text{Ph}_3\text{COO}^- + \text{Ph}_3\text{CCPh}_3 \rightleftharpoons \text{Ph}_3\text{COOCPh}_3 + \text{Ph}_3\text{C}^- \] (5)

The rate of reaction no longer depends exclusively on the dissociation rate since the triphenylmethyl radical is also produced by a direct attack of the triphenylmethyl peroxo radical on the original compound. The reaction with nitric oxide, however, apparently gives a good measure of the rate of dissociation of the original substance.\(^5\)

In 1911, Piccard reported that solutions of the Gomberg compound did not obey the Beer-Lambert law.\(^6\) This supported the equilibrium proposed by Gomberg and Cone.\(^2a\) In the case of this equilibrium (Equation 1), at greater dilutions, more of the original compound will dissociate to form triphenylmethyl radicals as a consequence of the law of mass action. While the relationship of the number of moles of Gomberg compound dissolved per liter of solution to absorbance of the solution is not linear, the relationship of the triphenylmethyl radical concentration to absorbance is linear. This behavior of triphenylmethyl radical solutions was used by Ziegler and Ewald to determine the extinction coefficient of the triphenylmethyl radical as well as the equilibrium constant for the process previously shown in Equation 1.\(^7\)

Ziegler and Ewald measured the extinction of a number of solutions of the Gomberg compound.\(^7\) At high dilutions, the extinction was found to approach a constant value. This value is the extinction of the triphenylmethyl radical. By extrapolating their data to infinite dilution, Ziegler and Ewald were able to obtain a value for the extinction coefficient of the triphenylmethyl radical. From
these values, together with the known original quantity of Gomberg compound used to prepare the solutions, a calculation of the equilibrium constant was possible. An equation for such a calculation may be written as shown in Equation 6.

\[
K = \frac{[R^*]^2}{[D]_0 - ([R^*]/2)}
\]  

(6)

In this equation, \([R^*]\) is the radical concentration and \([D]_0\) is the moles of Gomberg compound dissolved per liter of solution. The denominator represents the concentration of original compound remaining after the equilibrium has been established. Table 1 gives the values reported by Ziegler and Ewald using this method.\(^7\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(K \times 10^4) ((20^\circ C))</th>
<th>(\Delta H) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propionitrile</td>
<td>1.2</td>
<td>11.1</td>
</tr>
<tr>
<td>Ethyl benzoate</td>
<td>1.67</td>
<td>12.0</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>1.70</td>
<td>11.5</td>
</tr>
<tr>
<td>Dioxane</td>
<td>2.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>3.7</td>
<td>11.5</td>
</tr>
<tr>
<td>Ethylene Bromide</td>
<td>3.9</td>
<td>11.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Chloroform</td>
<td>6.9</td>
<td>10.5</td>
</tr>
<tr>
<td>Carbon Disulfide</td>
<td>19.2</td>
<td>11.0</td>
</tr>
</tbody>
</table>

There exist two potential sources of error in this type of determination other than the normal errors associated with spectrophotometry. The first is the sensitivity of the radical solutions to oxygen. This may cause errors by lowering the radical concentration of a solution which in turn lowers the Gomberg compound concentration. The second potential error is the reported photosensitivity of the Gomberg dimer.
It has been observed that upon exposure to light, the compound may disproportionate to triphenylmethane and a hydrocarbon residue.\(^8\) This would also reduce the concentration of radical in solution which again would cause inaccuracies in the determination of the extinction coefficient and the equilibrium constant. Although similar compounds have been observed to decrease in radical concentration spontaneously, especially at elevated temperatures, the Gomberg compound is not overly sensitive in this respect.\(^9,10\) It is interesting to note that the disappearance of radicals in these solutions was not always accompanied by a simultaneous decrease in the intensity of the color of the solutions.

Since the radical has an unpaired electron, it is a paramagnetic species. As such, its presence as well as a quantitative measure of its concentration may be obtained by magnetic susceptibility measurements. Several workers have made such measurements on solutions of the Gomberg compound.\(^9,11\) Reasonably good agreement between these measurements indicates that the experimental technique of each was satisfactory, even though the values so obtained were only half as large as the corresponding values determined by Ziegler, et al.,\(^4\) using the spectrophotometric technique.

The reason for the discrepancy between the values determined by the magnetic susceptibility and colorimetric methods is not clearly understood. The magnetic method is based on the fact that paramagnetic compounds are attracted by a magnetic field. Diamagnetic compounds, having no unpaired electron, are repelled by a magnetic field. For a solution containing a paramagnetic species, a diamagnetic species, and solvent, there will be a contribution from each which contributes to the overall observable value. The solvent diamagnetic
contribution may be experimentally measured and subtracted from the observed magnetic susceptibility of the solution. The diamagnetic contribution for the compounds being studied may be calculated using a table of empirical constants determined by Pascal.\textsuperscript{12} These constants depend on the atoms involved as well as the manner in which they are bonded to each other. The previous work using magnetic susceptibility measurements to determine the equilibrium constant for the Gomberg compound in solution has assumed that the hexaphenylethane structure assigned to the compound by Gomberg is correct. The previous work further assumes that the change from quadrivalent carbon in the Gomberg compound to trivalent carbon in the triphenylmethyl radical has no effect on the observed susceptibility of the solution except for the presence of the odd electron in the triphenylmethyl radical.

The correct structure of the compound Gomberg isolated was proposed by Jacobsen,\textsuperscript{13} but only recently shown to be correct by Lankamp, Nauta, and MacLean\textsuperscript{14} and others.\textsuperscript{15} It is not hexaphenylethane, but rather 4-triphenylmethyl-1-diphenylmethylene-2,6-cyclohexadiene, D, shown below.

\[
\begin{array}{c}
\text{Ph}_3\text{C} \ activation \ indicates \ substitution.
\end{array}
\]

The magnetic susceptibility determinations previously mentioned used the incorrect structure, hexaphenylethane, to calculate the diamagnetic correction for the undissociated Gomberg compound.

New equilibrium constants may now be calculated using the correct structure in the following manner. The diamagnetic contribution may be
approximated by the following expression in which the diamagnetic contribution, $M_x$, is equal to the sum of the product of the number of atoms of type $i$, $n_i$, and the Pascal constant of atoms of type $i$, $\lambda_i$.

$$M_x = \sum n_i \lambda_i + \lambda$$  \hspace{1cm} (7)

The Pascal constants for the atoms and structures needed for this calculation are given in Table 2.\textsuperscript{12} The $\lambda$ term in Equation 7 is a term to correct for special structural features.

\begin{table}
\label{table1}
Pascal's Constants
\begin{align*}
m_{\text{carbon}} &= -6.0 \times 10^{-6} \\
m_{\text{hydrogen}} &= -2.93 \times 10^{-6} \\
\lambda_{\text{benzene}} &= -1.5 \times 10^{-6} \\
\lambda_{\text{cyclohexane}} &= -3.0 \times 10^{-6} \\
\lambda_{\text{ethylene}} &= +5.5 \times 10^{-6}
\end{align*}
\end{table}

The diamagnetic contribution may now be calculated. The methylene-cyclohexadiene system will be treated as a cyclohexane and three ethylenes.

$$M_D = [38(-6.0) + 30(-2.93) + 6(-1.5) + (-3.0) +$$
$$3(+5.5)] \times 10^{-6}$$  \hspace{1cm} (8)

$$M_D = -311.4 \times 10^{-6}$$

Previously, a value for $M_D$ of $-324 \times 10^{-6}$ was obtained by using the incorrect structure, hexaphenylethene.\textsuperscript{9,11} There is obviously a significant difference in these two values.
The observed susceptibility is the sum of the individual susceptibilities of a solution. This may be stated as shown in Equation 9.

\[
X = x_1p_1 + x_2p_2 + \ldots + x_np_n
\]  

(9)

In this expression, \( x_n \) is the observed susceptibility for compound \( n \), and \( p_n \) is the weight fraction of compound \( n \). Using this expression, it is possible to calculate the susceptibility of \( D \) in solution from previously obtained experimental values of \(-0.708 \times 10^{-6}\) for the solvent benzene and \(-0.700 \times 10^{-6}\) for a solution with \( p_D = .0549 \).

\[
X_M = (X_D)(M_D)
\]  

(11)

\[
X_M = (0.56228 \times 10^{-6})(486 \text{ gm/mole})
\]

\[
X_M = -273.27 \times 10^{-6}
\]

The molar paramagnetism of free radicals in this solution may be obtained as shown in Equation 13.

\[
(-273.27 \times 10^{-6}) - (-311.4 \times 10^{-6}) = 38.13 \times 10^{-6}
\]  

(13)

Since total dissociation would give a molar paramagnetism of \( 2540 \times 10^{-6} \) at \( 20^\circ C \),\(^9,11\) the fraction dissociated may now be calculated.

\[
\frac{38.13 \times 10^{-6}}{2540 \times 10^{-6}} = 0.015
\]  

(14)
From the original equilibrium expression, Equation 6, one may obtain the following if $\alpha$ is the fraction of Gomberg dimer dissociated and $m$ is the stoichiometric Gomberg dimer concentration, $[D]_0$.

$$K = \frac{4\alpha^2 m}{1 - \alpha} \quad (15)$$

$$K = \frac{4(.015)^2(.10503)}{1 - .015} = 9.6 \times 10^{-5} \quad (16)$$

This value is in even worse agreement with the previously mentioned spectrophotometric value (Table 1). It is likely that the Pascal constants used to give the terms for the methylene cyclohexadiene system are not applicable to this system. It is also likely that the diamagnetic correction for the radical is important in this system, but no such correction for the change from quadrivalent carbon to a trivalent carbon may be found in the literature. The diamagnetic correction term is too low, as has been suggested in the past,\textsuperscript{16,17} but the term is too low by an unknown amount.

Paramagnetic resonance spectroscopy has also been used to measure the equilibrium constant for this system. The measurements have yielded equilibrium constants ranging from $2.92 \times 10^{-4}$ to $3.76 \times 10^{-4}$ at $20^\circ C$\textsuperscript{18}. Although the quantities so obtained are in somewhat better agreement with the spectrophotometric data, the spread of values reported indicates that the experimental variations in these measurements are significant. Paramagnetic resonance spectroscopic methods are known to be very sensitive, but not very suitable for precise determinations of the type needed for this system.

A new determination of this equilibrium constant by a spectrophotometric method has been one purpose of this work. By utilizing an
automated sampling system, the problems of oxygen exposure and photochemical decomposition of the sample were avoided. The use of a high quality spectrophotometer in conjunction with the automated sampling system has made possible a determination of high precision and accuracy.

While involved in the study of the reaction of thiophenol with the triphenylmethyl radical, Lewis and Butler observed that at low temperatures, the disappearance of color of a solution of thiophenol and triphenylmethyl radical in toluene was slow. A rate constant for this reaction was estimated to be of the order of $10^0 \text{ M}^{-1}\text{sec}^{-1}$ based on a visual estimate of the rate of color disappearance. A second objective for this project has been the careful measurement of this reaction rate employing an automatic sampling system in conjunction with a recording spectrophotometer.
Results and Discussion

The measurement of the equilibrium constant for the dissociation of the Gomber dimer depended upon careful isolation of the dimer. By weighing out a quantity of Gomberg dimer, dissolving it in purified solvent and measuring the absorbance of the solution at different concentrations, the equilibrium constant has been determined.

The system may be described by the following.

\[
\begin{align*}
\text{Ph}_3\text{C}^- & \overset{k_1}{\rightleftharpoons} \text{Ph}_3\text{C}^+ + \text{Ph}_3\text{C}^- \\
\end{align*}
\]  \hspace{1cm} (17)

If D represents the Gomberg dimer, and R' represents the triphenylmethyl radical, the equilibrium constant may be expressed as shown in Equation 18.

\[
K = \frac{k_1}{k_{-1}} = \frac{[R']^2}{[D]} \hspace{1cm} (18)
\]

The denominator \([D]\) is related to the total stoichiometric concentration of Gomberg dimer, \([D]_0\), by the following expression.

\[
[D] = [D]_0 - \frac{[R']}{2} \hspace{1cm} (19)
\]

The quantity \([R']/2\) represents the quantity of Gomberg dimer which has dissociated, the factor of two arising from the equilibrium stoichiometry.

The Beer-Lambert law allows the calculation of the concentration of radicals in solution from the absorbance of the solution as shown in Equation 20.
\[ A = e_l c \]  \hspace{1cm} (20)

\[ [R^+] = \frac{A_R}{c_R} \]  \hspace{1cm} (21)

In this expression, \( e_R \) is the extinction coefficient of the triphenylmethyl radical, \( l \) is the path length in centimeters, and \( A_R \) is the absorbance due to the radical. The cell length here is one cm.

Substituting Equation 21 into Equation 18 yields Equation 22.

\[ K = \frac{[R^+]^2}{[D]_o - ([R^+] / 2)} = \frac{(A/e)^2}{[D]_o - (A/[2e])] \]  \hspace{1cm} (22)

This expression may be algebraically converted to the form shown in Equation 23.

\[ \frac{[D]}{A} = \frac{1}{Ke^2} A + \frac{1}{2e} \]  \hspace{1cm} (23)

Thus a plot of the total stoichiometric concentration of the Gomberg dimer divided by the absorbance versus the absorbance gives a line of slope \((Ke^2)^{-1}\) and intercept \((2e)^{-1}\). This type of plot not only gives the extinction coefficient, but also the equilibrium constant for this system. Deviations from linearity of such plots immediately render the information that the data is of poor quality or a nonequilibrium process is being observed. The use of such a treatment depends on time being allowed after sample preparation for equilibration.
Such a treatment relies on the precise knowledge of the initial stoichiometric Gomberg dimer concentration, \([D]_0\). Although some workers have relied upon the assumption that the reaction of mercury or silver with triphenylmethyl chloride gives a nearly quantitative yield of the triphenylmethyl radical and hence Gomberg dimer,\(^{11,18b}\) it was decided not to rely upon this assumption in this work. Solutions of the radical may be analyzed by several methods in order to determine the concentration of Gomberg dimer. Hammond, Roove, and Modic developed an analysis in which the triphenylmethyl radical solution is treated with an excess of benzoyl peroxide, then the excess benzoyl peroxide determined iodometrically.\(^{20}\) A second method in which the solution is allowed to react with oxygen or nitric oxide also gives a measure of the original Gomberg dimer concentration.\(^{3,11c,18b}\) Either the volume of gas absorbed may be monitored or the solid product isolated and weighed. Each of these analytical techniques is somewhat cumbersome. The most reliable method appears to be the isolation of the Gomberg dimer in a state of high purity, then preparing solutions from this material.

The automatic sampling system made many determinations possible from each solution prepared. Each determination could be performed on a solution of precisely selected concentration of Gomberg dimer by causing the sampling system to dilute the original solution by a predetermined amount. The absorbance of the radical at 516 nm was measured and used in the subsequent calculations. Figures 1-5 give the Equation 23 plots of the experimental data at the temperatures employed, \(-5^\circ\text{C} \text{ to } 30^\circ\text{C}\). The extinction coefficient is given on the plots as well as the extinction coefficient of the radical at 516 nm.
$K = 5.91 \times 10^{-4}$

$e = 650$

**Figure 1**

The [D]₀/A Versus A Plot of Gomberg Dimer at 30°C in Toluene
Figure 2
The \([D]_0/A\) Versus A Plot of Gomberg Dimer at 20°C in Toluene

\[ K = 3.08 \times 10^{-4} \]
\[ e = 663 \]
Figure 3

The [D]/A Versus A Plot of Gomberg Dimer at 10°C in Toluene

\[ K = 1.47 \times 10^{-4} \]

\[ \epsilon = 660 \]
Figure 4

The $[D]_o/A$ versus $A$ plot of Gomberg dimer at 0°C in Toluene

$K = 0.791 \times 10^{-4}$

$\varepsilon = 665$
Figure 5

The $[D]_0/A$ Versus $A$ Plot of Gomberg Dimer at -5°C in Toluene
The slope and intercept for each was calculated using the method of least squares. Each of the plots is a collection of experimental determinations involving several different original solutions of the Gomberg dimer. The linearity obtained using these different original solutions is indicative of the purity of the isolated Gomberg dimer used to prepare the solutions. For comparison, a plot of this type of the data of Ziegler and Ewald\textsuperscript{7} is given in Figure 6. The values obtained from their data using this method do not differ significantly from the values they originally reported. The values shown in Figure 6 were those obtained by the least squares fit described previously. The deviation of the high absorbance value from the linear fit of the other values is thought to be due to their method of measuring high absorbances by measuring the absorbance at 522 nm (the steeply rising portion of the 516 nm peak), then calculating the 516 nm absorbance from this 522 nm measurement. A sizeable error would be expected in such a method when the peak is large and the sides steep as is the case for high absorbances.

From magnetic susceptibility measurements,\textsuperscript{9,11c} there is an indication that the equilibrium constant in toluene solutions should be approximately 73% as large as the equilibrium constant in benzene. If this is correct, then the value of the equilibrium constant obtained by Ziegler and Ewald\textsuperscript{7} in benzene solution may be used to calculate the equilibrium constant in toluene solution. Such a calculation predicts that the value in toluene solution should be $3.0 \times 10^{-4}$ which is in good agreement with the value obtained in this work.

From the equilibrium constants obtained for the different temperatures, it is possible to calculate the enthalpy of reaction, free
Figure 6

The [D]_o/A Versus A Plot of Gomberg Dimer in Benzene at 20°C from the Data of Ziegler and Ewald

K = 4.14 x 10^{-4}
e = 661
energy and entropy change for the equilibrium process. These values were obtained from the least squares fit of the plot of the natural logarithm of the equilibrium constants versus the reciprocal of the absolute temperature. This plot is shown in Figure 7 and the values so obtained are shown in Table 3.

**TABLE 3**

Values Obtained for Triphenylmethyl in Toluene

| H = 11.24 kcal/mole | \( K_{20} = 3.08 \times 10^{-4} \) |
| S = 22.14 cal/°C | \( F_{20} = 4.71_0 \) kcal/mole |

Table 4 gives the corresponding values determined by Ziegler and Ewald\(^7\) in benzene solution.

**TABLE 4**

Values Obtained for Triphenylmethyl in Benzene\(^7\)

| H = 11.3 kcal/mole | \( K_{20} = 4.1 \times 10^{-4} \) |
| S = 22.9 cal/°C | \( F_{20} = 4.54 \) kcal/mole |
Figure 7

The Relationship Between the Triphenylmethyl Equilibrium Constant and Temperature in Toluene Solution
The reaction of triphenylmethyl radical with thiophenol is fairly complex. The following scheme shows the possible course of reactions in this system.

\[ D \xrightarrow{k_1} R^+ + R^- \]  \hspace{1cm} (24)

\[ R^+ + \text{PhSH} \xrightarrow{k_2} \text{RH} + \text{PhS}^- \]  \hspace{1cm} (25)

\[ D + \text{PhS}^- \xrightarrow{k_3} D^- + \text{PhSH} \]  \hspace{1cm} (26)

\[ D^- + \text{PhSH} \xrightarrow{k_4} D^- + \text{PhS}^- \]  \hspace{1cm} (27)

\[ \text{PhS}^- + R^- \xrightarrow{k_5} \text{RSPh} \]  \hspace{1cm} (28)

In this scheme, D represents the Gomberg dimer, R' the triphenylmethyl radical, PhSH is thiophenol, \text{PhS}' is the phenyl thiy1 radical, and RH is triphenylmethane. The compound represented by D' is the hydrocarbon shown below.\textsuperscript{19}

\[ \text{Ph}_3\text{C} - \text{C} - \text{Ph} \]

The reaction in Equation 25 is as follows.

\[ \text{Ph}_3\text{C} - \text{CPh}_2 + \text{PhS}' \xrightarrow{k_3, k_{-3}} \text{PhSH} + \text{Ph}_3\text{C} - \text{CPh}_2 \]
The overall rate expression of disappearance of the triphenylmethyl radical may then be written as shown in Equation 30.

\[
\frac{-d[R^\cdot]}{dt} = 2k_{-1}[R^\cdot]^2 - 2k_1[D] + k_2[R^\cdot][PhSH] - k_{-2}[RH][PhS^\cdot] + k_5[R^\cdot][PhS^\cdot] - k_{-5}[RSPh]
\]  

(31)

It should be noticed that Equations 26 and 27 do not appear in this expression. They have been neglected since in previous work the D1 hydrocarbon was not observed as a reaction product except when dilute solutions of triphenylmethyl radical relative to thiophenol were employed at low temperatures.\textsuperscript{19} It would seem that the breakdown of triphenylmethyl phenyl sulfide is unlikely at the temperatures involved and hence may be neglected.\textsuperscript{20}

Assuming that Reaction 25 is not reversible on the time scale involved, and assuming a steady state in phenylthiyl radicals is achieved, Equation 31 may be written.

\[
k_2[R^\cdot][PhSH] = k_5[R^\cdot][PhS^\cdot]
\]  

(31)

The steady state concentration of phenylthiyl radicals may now be written as shown in Equation 32.

\[
[PhS^\cdot] = \frac{k_2[R^\cdot][PhSH]}{k_5[R^\cdot]} = \frac{k_2[PhSH]}{k_5}
\]  

(32)

Equation 30, together with Equation 32, now gives the overall expression for the rate of disappearance of R\' with time. (Equation 33).
\[
\frac{-d[R^*]}{dt} = 2k_{-1}[R^*]^2 - 2k_{-1}[D] + k_2[R^*][PhSH] + \frac{k_5[R^*]k_2[PhSH]}{k_5}
\]

(33a)

\[
\frac{-d[R^*]}{dt} = 2k_{-1}[R^*]^2 - 2k_1[D] + 2k_2[R^*][PhSH]
\]

(33b)

If the initial equilibrium is fast on the time scale involved, Equation 33b reduces to a second order expression as shown in Equation 34.

\[
\frac{-d[R^*]}{dt} = 2k_2[R^*][PhSH]
\]

(34)

Upon performing the indicated experiments by mixing solutions of Gomberg dimer in toluene with solutions of thiophenol in toluene, it was found that the disappearance of triphenylmethyl radical with time as the reaction proceeded did not follow this second order expression. This led to the conclusion that the initial equilibrium reaction (Equation 24) is not fast relative to the hydrogen transfer reaction. The actual rate expression must then be written as Equation 33b. The rate of disappearance of Gomberg dimer and thiophenol may be written as shown in Equations 35 and 36, respectively.

\[
\frac{-d[D]}{dt} = k_1[D] - k_{-1}[R^*]^2
\]

(35)
\[-\frac{d[\text{PhSH}]}{dt} = k_2[R^\cdot][\text{PhSH}] \]  \hspace{1cm} (36)

These equations (Equations 33b, 35, and 36) may be rewritten in terms of finite concentration changes over finite time intervals as shown in Equations 37, 38, and 39.

\[-\frac{\Delta[R^\cdot]}{\Delta t} = 2k_{-1}[R^\cdot]^2 - 2k_1[D] + 2k_2[R^\cdot][\text{PhSH}] \]  \hspace{1cm} (37)

\[-\frac{\Delta[D]}{\Delta t} = k_1[D] - k_{-1}[R^\cdot]^2 \]  \hspace{1cm} (38)

\[-\frac{\Delta[\text{PhSH}]}{\Delta t} = k_2[R^\cdot][\text{PhSH}] \]  \hspace{1cm} (39)

These expressions may be rearranged and generalized to give Equations 40, 41, and 42.

\[ [R^\cdot]_{t+\Delta t} = [R^\cdot]_t + (-2k_{-1}[R^\cdot]^2_t + 2k_1[D]_t - 2k_2[R^\cdot]_t[\text{PhSH}]_t)\Delta t \]  \hspace{1cm} (40)

\[ [D]_{t+\Delta t} = [D]_t + (-k_1[D]_t + k_{-1}[R^\cdot]^2_t)\Delta t \]  \hspace{1cm} (41)

\[ [\text{PhSH}]_{t+\Delta t} = [\text{PhSH}]_t + (-k_2[R^\cdot]_t[\text{PhSH}]_t)\Delta t \]  \hspace{1cm} (42)

From the literature values of \(k_1\) and \(k_{-1}\), these may be used to calculate the concentration at time \(t\) of each of the species present.
for an estimated value of \( k_2 \). By using the experimental values for 
\([D]_0\) and \([\text{PhSH}]_0\), it is then possible to duplicate the experimentally
observed behavior of \([R']\) as a function of time.

A computer program was used to generate values of \([R']_c\) which
were compared to the experimentally determined values. This treat-
ment used Equations 40, 41, and 42 to calculate the triphenylmethyl
concentrations at time \( t \) as discussed previously. The literature
values of \( k_1 \) and \( k_{-1} \) had been determined using benzene solutions.\(^5\)
These values were corrected by assuming that the solvent effect on
the equilibrium constant was a result of a change in the dissociation
rate constant \( k_1 \). The corrections made were such that the \( k_1 \) to \( k_{-1} \)
ratio gave values equal to the equilibrium constants determined in
this work in toluene solutions. The literature values of \( k_1 \) as well
as the corrected values of \( k_1 \) are presented in Table 5 along with
the literature values of \( K \) and \( k_{-1} \) and the values of \( K \) determined
in this work.

\[
\text{TABLE 5}
\]

<table>
<thead>
<tr>
<th>( T(\degree C) )</th>
<th>( K^a(10^4) )</th>
<th>( K^b(10^4) )</th>
<th>( k_{-1}^c(M^{-1}\text{sec}^{-1}) )</th>
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<th>( k_{1}^e(\text{sec}^{-1}) )</th>
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</tr>
</tbody>
</table>

\(^a\)Ziegler and Ewald\(^4\) in benzene

\(^b\)this work

\(^c\)Ziegler, et al.\(^5\)

\(^d\)Calculated from \( K^a \) and \( k_{-1} \)

\(^e\)Calculated from \( K^b \) and \( k_{-1} \)

\(^f\)Calculated from \( \Delta H \) (Table 3)
Good agreement with the experimentally observed values was obtained when \( k_2 \) was correctly estimated. As in the determination of the equilibrium constant, the triphenylmethyl radical absorption at 516 nm was followed as a function of time. A typical set of experimental values is shown in Figure 8 along with the values for several \( k_2 \) estimates. From this figure, it is apparent that an erroneous value for \( k_2 \) may be easily detected. Table 6 gives the values of the second order rate constant, \( k_2 \), determined by this method at the temperatures and concentrations involved.

In order to insure that the reaction followed was actually the hydrogen transfer, the experiments were repeated with deuterated thiophenol. Since the observed rates are slower for deuterated thiophenol, the determining step is the hydrogen transfer reaction (Equation 25). The rate constants obtained for the deuterated thiophenol reaction with triphenylmethyl are displayed in Table 7 along with the initial concentrations and the temperatures at which these measurements were made.

The energy of activation for the reaction with thiophenol and deuterated thiophenol have been calculated to be 9.06 kcal/mole and 10.60 kcal/mole, respectively. Tables 6 and 7 display the values of \( k_2 \) calculated at each temperature which give the best linear fit to the experimental values. These were obtained by a least squares fitting method applied to the plot of the natural logarithm of the rate constants versus the reciprocal of the absolute temperature.

A tritium isotope effect for the reaction of thiophenol with triphenylmethyl in toluene has been reported by Lewis and Butler. The difference in activation energies for the reaction with thiophenol and tritiated thiophenol was found to be 2590 cal/mole over the range
Figure 8

Typical plot of Absorbance Versus Time for Observed and Calculated Values of Triphenylmethyl Concentration in its Reaction with Thiophenol in Toluene
### TABLE 6

Rate Constants for the Hydrogen Transfer Reaction\(^{a}\)

<table>
<thead>
<tr>
<th>Initial Concentrations</th>
<th>(k_2^b) ((M^{-1}\text{sec}^{-1}))</th>
<th>(k_2^d) ((M^{-1}\text{sec}^{-1}))</th>
<th>(T^c) (\degree\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([D]_0) 0.009104</td>
<td>0.00087</td>
<td>14.0</td>
<td>12.52</td>
</tr>
<tr>
<td>([\text{PhSH}]_0) 0.004571</td>
<td>0.00312</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>0.004565</td>
<td>0.00308</td>
<td>4.43</td>
<td>4.62</td>
</tr>
<tr>
<td>0.006140</td>
<td>0.00267</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>0.007755</td>
<td>0.00154</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>0.009062</td>
<td>0.00077</td>
<td>4.77</td>
<td></td>
</tr>
<tr>
<td>0.004540</td>
<td>0.00309</td>
<td>2.23</td>
<td>2.676</td>
</tr>
<tr>
<td>0.006471</td>
<td>0.00231</td>
<td>2.44</td>
<td></td>
</tr>
<tr>
<td>0.007780</td>
<td>0.00154</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>0.008911</td>
<td>0.00081</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>0.004556</td>
<td>0.00305</td>
<td>1.63</td>
<td>1.484</td>
</tr>
<tr>
<td>0.005134</td>
<td>0.00253</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>0.007767</td>
<td>0.00152</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>0.009109</td>
<td>0.00087</td>
<td>1.64</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Each entry represents two experimental determinations.

\(^{b}\)Calculated from the values of \(k_1\), \(k_{-1}\), \([D]_0\), and \([\text{PhSH}]_0\) for the best fit of the experimental data by the use of Equations 40, 41, and 42.

\(^{c}\)Temperature regulation of the reaction mixtures was maintained at within 0.1\degree C of the indicated temperature except in the case of the 0\degree C experiments where it was maintained to within 0.2\degree C.

\(^{d}\)Calculated from the best fitting Arrhenius equation.
TABLE 7

Rate Constants for the Deuterium Transfer Reaction\(^a\)

<table>
<thead>
<tr>
<th>Initial Concentrations</th>
<th>([\text{D}_2]_0)</th>
<th>([\text{PhSD}]_0)</th>
<th>(k_2^b) ((\text{M}^{-1}\text{sec}^{-1}))</th>
<th>(k_2^d) ((\text{M}^{-1}\text{sec}^{-1}))</th>
<th>(T^c) (({}^\circ\text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004431</td>
<td>0.00312</td>
<td>3.01</td>
<td>2.74</td>
<td></td>
<td>40</td>
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<tr>
<td>0.007732</td>
<td>0.00147</td>
<td>2.73</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>0.004412</td>
<td>0.00407</td>
<td>0.862</td>
<td>.7331</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>0.005253</td>
<td>0.00234</td>
<td>0.858</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>0.008137</td>
<td>0.00063</td>
<td>0.864</td>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>0.004571</td>
<td>0.00423</td>
<td>0.406</td>
<td>.452</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.005270</td>
<td>0.00242</td>
<td>0.409</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.009101</td>
<td>0.00098</td>
<td>0.407</td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.004631</td>
<td>0.00394</td>
<td>0.246</td>
<td>.227</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.009175</td>
<td>0.00991</td>
<td>0.245</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.007936</td>
<td>0.00150</td>
<td>0.243</td>
<td></td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Each entry represents two experimental determinations.

\(^b\)Calculated from the values of \(k_1\), \(k_{-1}\), \([\text{D}_2]_0\), \([\text{PhSD}]_0\) by the use of equations 40, 41, and 42 for the best fit of the observed data.

\(^c\)Temperature regulation of the reaction mixtures was better than \(+0.1^\circ\text{C}\) except at 0\(^\circ\text{C}\) where regulation was better than \(+0.2^\circ\text{C}\).
of temperatures 0°C to 40°C. The ratio of pre-exponential factors for the reaction with thiophenol and tritiated thiophenol was found to be 0.187. If the Swain equation\textsuperscript{21} is applied to the $k_H/k_T$ values reported by Lewis and Butler,\textsuperscript{19} values for $k_H/k_D$ may be obtained. The values calculated by this method are shown in Table 8 along with the experimentally determined values of $k_H/k_D$.

TABLE 8
Deuterium Isotope Effects for the Hydrogen Transfer Reaction

<table>
<thead>
<tr>
<th>$k_H^a/k_D^b$</th>
<th>$k_H^a/k_D^b$</th>
<th>$T(°C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.72</td>
<td>5.60</td>
<td>40</td>
</tr>
<tr>
<td>5.33</td>
<td>6.82</td>
<td>20</td>
</tr>
<tr>
<td>5.81</td>
<td>7.61</td>
<td>10</td>
</tr>
<tr>
<td>6.60</td>
<td>8.60</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated from average values for each temperature using the values of Tables 6 and 7

\textsuperscript{b}Calculated from the tritium isotopes of Lewis and Butler using the Swain equation

It will be noticed that the experimental values of $k_H/k_D$ are lower than the values calculated by the previously described method from the literature values for $k_H/k_T$. The actual values of $k_H/k_D$ are somewhat higher than the experimentally determined values. The thiophenol employed in the measurements of the rate of reaction with deuterated thiophenol was deuterated to an extent of 92%. The 8% impurity of thiophenol caused the observed rates of reaction with triphenylmethyl to be faster than they would have been if the
thiophenol had been 100% deuterated. This causes an error in the calculated values of \( k_H/k_D \). If the reactions had been followed to small extents of completion, the observed rate constants could be corrected for the protium impurity. The reactions were followed to large extents of completion, however, rendering such corrections unreliable.

Another explanation for the low values of the deuterium isotope effects observed is found in the uncertainty in the pre-exponential factor in the equation given by Lewis and Butler.\(^\text{19}\)

\[
\frac{k_H}{k_T} = 0.187\exp[2590/(RT)] \tag{43}
\]

This equation may be derived from the division of Equation 44 by Equation 45 to obtain an equation of the form of Equation 46.

\[
k_H = A_H \exp[-E_H/(RT)] \tag{44}
\]

\[
k_T = A_T \exp[-E_T/(RT)] \tag{45}
\]

\[
\frac{k_H}{k_T} = \frac{A_H}{A_T} \exp[-(E_H-E_T)/(RT)] \tag{46}
\]

If the observed isotope effect is due only to the difference in zero-point energy of the reactants and the transition state, the Swain equation (Equation 47) gives good agreement between experimentally observed isotope effects and calculated isotope effects.\(^\text{21}\)
\[
\frac{k_H}{k_T} = \left(\frac{k_H}{k_D}\right)^{1.442}
\]  

(47)

In this case, however, Lewis and Butler have calculated that such behavior at 25°C would result in \(k_H/k_T\) of 11.5 which is significantly lower than the value which they observed experimentally \((k_H/k_T = 14.8)\). Since the Swain equation is meant to be applied in cases where \(A_H/A_T = 1\), and since Lewis and Butler have shown that this system is not such a case, perhaps the Swain equation is not applicable.

A final point to be mentioned in connection with this work is that of a potential systematic error in the rate measurements. Such an error is indicated by the poor fit of the observed rate data to an Arrhenius relationship. Several sources of this error are present in these determinations. The assumptions involved in the conversion of the literature values of \(k_1\) to the toluene system may not be valid. The plotting method itself requires that a qualitative decision be made as to whether the fit of a particular set of calculated \([R^1]\) is in fact sufficiently good. In this technique, mixing errors or temperature errors immediately after mixing of the solutions may be significant. It is estimated that the uncertainty in these rate measurements is less than ±10%. It should be noted that such an error reduces the difference in the observed \(k_H/k_D\) by a significant amount.

The literature contains few examples of hydrogen abstraction reactions involving free radicals and thiols for which absolute reaction rate constants are known. Inabe and Darwent have reported the rate of hydrogen radicals reacting with methyl mercaptan to be \(4 \times 10^8 \text{ M}^{-1}\text{sec}^{-1}\) in the gas phase. Studies more closely related to
the system of this work have been reported by Prior and Kneipp\textsuperscript{23} and by Russell.\textsuperscript{24} They have found the rate of the reaction between diphenylpicrylhydrazyl (DPPH), and \textit{tert}-butyl mercaptan to be $4 \times 10^{-4} \text{ M}^{-1}\text{sec}^{-1}$. It may be seen that the absolute reaction rate constant for the reaction of triphenylmethyl with thiophenol in toluene as determined by this work falls within this range.
Experimental

Materials and Methods

The automatic sampling system described previously was employed in sample preparation. A Cary 14 recording spectrophotometer was employed to measure the absorption spectra of the samples. Samples were thermostatted at each temperature by the use of an external Haake circulator bath. At temperatures below 30°C, a refrigeration unit constructed by M. M. Butler was used to maintain good regulation. Sample temperatures were monitored by the use of a thermistor placed in the sample cell. The resistance of this thermistor gave a good measure of the sample temperature. The resistance of the thermistor was determined by the use of a Wheatstone bridge and galvinometer. The resistance was used to determine the temperature by the use of the relation in Equation 48. For R in ohms and T in °Kelvin, the following may be used.

\[ R = B \exp(b/T) \]  \hspace{1cm} (48)

For the particular thermistor used in this work, the two constants had the values; \( B = 0.012065 \), \( b = 3369.93 \) as determined experimentally.

Triphenylmethyl chloride obtained from Aldrich Chemical Co. was recrystallized from acetyl chloride. The white solid so obtained was collected on a sintered glass filter, washed with dry diethyl ether, and quickly transferred to a vacuum desicator. After evacuating the desicator for twelve hours, the desicator was filled with argon gas and sealed for storage of the material. The melting range of this material was 113-114°C (uncorr.) (lit. 112.5-113°C\(^2\)). When the melting range exceeded 1°C, the recrystallization was repeated.
Reagent grade toluene (Matheson, Coleman, and Bell) was dried for seven days over 4A molecular sieves (Linde), then decanted into a dry flask containing sodium wire. Immediately before using, the toluene was degassed by the freeze-thaw method three times, then distilled by a conventional bulb to bulb technique.

Reagent grade acetone was refluxed with potassium permanganate until added permanganate caused the solution to remain violet in color. The acetone was distilled onto 4A molecular sieves (Linde) under an atmosphere of nitrogen gas. Immediately before use, the acetone was decanted into a round bottomed flask, degassed, and bulb to bulb distilled after the manner of the toluene described previously.

1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.

Mercury (46 gm, 0.228 mole) was added to a solution of 15.9 gm (0.057 mole) of triphenylmethyl chloride in 150 ml of purified acetone. This was magnetically stirred overnight, filtered to remove excess mercury and mercuric chloride, and concentrated to 40 ml by means of a mechanical vacuum pump. The resulting solid was collected on a sintered glass filter. After recrystallizing in similar manner six times from purified acetone, the white solid was stored in an evacuated ampoule, m.p. 152-153°C(uncorr) (lit. 153.3-154°C). The above procedure was carried out in a glove bag after thoroughly purging with argon gas six times. Due to the possible light sensitivity of the triphenylmethyl radical in solution, the above procedure was performed in a darkened room. This procedure is an adaptation of that used by Leftin and Lichtin.25

Thiophenol. Reagent grade thiophenol was dried over 4A molecular sieves (Linde) for ten days. The thiophenol was then decanted into a round bottomed flask and distilled under a nitrogen atmosphere taking
only a small middle fraction. This procedure was repeated twice, each time taking only the middle fraction. The final distillation gives material of b.p. 168.5-169°C (uncorr).

Thiophenol-Deuterium Labeled. Thiophenol was refluxed with 98% D_2O for three hours, the D_2O distilled out, and the procedure repeated three times with fresh 98% D_2O. The thiophenol was then dried over magnesium sulfate (anhydrous) for 24 hours and distilled as described previously for thiophenol.

General Procedure for the Preparation of Solutions for the Sampling System. The reservoirs were placed in a glove bag along with the solvents to be used and the thiophenol or triphenylmethyl dimer container. In the case of dimer solution preparation, an estimated amount of the solid dimer was transferred into a tared, evacuable ampoule. This ampoule was then evacuated and sealed, removed from the glove bag and weighed. The ampoule was then placed in the glove bag again, the glove bag repurged with argon gas, and the solid dissolved in the required amount of solvent. The solution was then placed in the system reservoir, sealed, and removed from the glove bag. The reservoir was then connected to the system. Thiophenol solutions were prepared by a similar procedure.

Gas Purge. Argon gas at a vigorous flow rate was used to continually sweep the Cary 14 cell compartment. Argon gas was also introduced into the sample at the bottom of the cell of one minute immediately following sample addition to ensure good mixing of the sample. The reservoirs were kept under an atmosphere of argon to prevent contamination of the solutions.

Initial Loading of the Sampling System. The reservoirs were attached to the proper syringe unit by way of ball and socket joints.
The modified reservoir-syringe valves were positioned to allow the syringes to expell their contained gas into the atmosphere upon delivery. A small metal tube connected to the purge gas supply was inserted into the valve exhaust orifice. A rapid flow of gas at this point was established. The syringe units were then caused to refill and deliver at least ten times. This acted to draw in purge gas at the valve orifice and expell it from the syringe tips. This rinsed all oxygen from the syringes. The reservoir-syringe valves were then opened to the reservoirs. The syringes were then caused to deliver and refill several times until liquid was expelled from the tips. The reservoir-syringe valve was again positioned to expell gas into the atmosphere. The syringe was given the deliver command while the deliver position valve microswitch was manually held in. This caused the syringe to expell the gas trapped in the reservoir line. When the liquid level in the reservoir line reached the syringe-reservoir valve, delivery was halted by releasing the valve microswitch and depressing the "clear" pushbutton momentarily. The reservoir-syringe valve was then opened to the reservoir. The sample system is now ready for use.

**Measurement Procedure**

Radical solution was delivered into the cell by presetting the quantity of solution desired on the sampling system preset encoders and depression of the "deliver" switch. Toluene was similarly preset and delivered. The total delivered volume was always less than 2.5 ml, the cell capacity. Each measurement was made after twice rinsing the cell with the preset solution concentration. The cell was then filled a third time and allowed to stabilize at the thermostat temperature.
This temperature was monitored by the cell thermistor as described previously. An absorption spectrum was then taken of the solution to check for stable spectrophotometer baseline and peak position. The absorption spectrum from 520 nm to 510 nm was then measured using a very slow scanning speed. This was rescanned three times as a check for any time dependence of the absorption. The numbers so obtained were then used along with the counts delivered from each syringe to calculate the extinction coefficient and equilibrium constant at the temperature investigated by the method described previously.

Measurement of the Rate of Reaction of Thiophenol with Triphenylmethyl

General Procedure

These measurements were made in the same manner as the previously described equilibrium measurements. One of the syringe units contained toluene solutions of triphenylmethyl and the other syringe contained a toluene solution of thiophenol. The solutions were mixed as before but in this case the absorbance as a function of time was recorded at 516 nm with frequent scans of the 700 nm to 300 nm range being made to ensure that the absorbance being recorded was in fact due to the radical. The solutions were found to require from one to two minutes for thermal equilibration depending upon the temperature being studied.
References

   (b) M. Gomberg, Chem. Ber., 33, 3150 (1900).
   (c) M. Gomberg, Chem. Ber., 39, 3287 (1904).


   (b) K. Ziegler, A. Seib, K. Knoevenagel, P. Herte, and F. Andreas, Justus Liebig's Ann. Chem., 551, 150 (1942).


    (d) E. Muller and I. Muller-Rodloff, Justus Liebig's Ann. Chem., 521, 89 (1936).


Parts List
for
the Automatic Sampling System

Power Supply

T - filament transformer, Stancor P-8358 12.6 vct
R1 - 60 ohm, 1/4w, 10% resistor
R2 - 2.2K ohm, 1/4w, 10% resistor
R3 - 750 ohm, 1/4w, 10%, resistor
R - 7 ohm, 25w, power resistor
RECT - full wave bridge rectifier, Motorola MDA 952-1
Q - 2N174 Power Transistor
C1 - 4000 uf, 30vdc, elec. cap.
C2 - 1 nf, 30vdc ceramic cap.
S - DPDT switch
F - 125vac, 1A fuse
IC - Fairchild uA723 regulator FU5R7723393

Comparator Strobe Control

D1-D6 - 1W3064 signal diode
R1-R6 - 1K ohm 1/4w, 10% resistor
Q1-Q3 - 2N2222 transistor

Counter Sequencer Interface

IC1-IC3 - Texas Inst. SN7472N JK Flip-flop
Q1-Q3 - 2N2222 transistor
R1-R9 - 1K ohm 1/4w, 10% resistor
RRL-RR3 - Potter and Brumfield JRM1000 reed relays
D1-D6 - 1W914 signal diode
C1 - .01 uf mylar cap.
Sequencer
RR1-RR4 - Potter and Brumfield JRM 1006 reed relay
SCR3-SCR8 - 2N4443 silicon controlled rectifier
SCR1,2 - C10602 silicon controlled rectifier
R - resistor 1/4w 5%, 11K ohm
D1-D6 - 1N3064 signal diodes
Display
IC1-IC4 - Monsanto MAN4A Light emitting diode, seven segment readouts
Decoder
IC1-IC4 - Monsanto MSD101 Decoder/drivers
Counter
IC1-IC4 - Texas Instr. SN74192N presettable up/down decade counters
Encoder
Q1-Q3 - 2N1711 transistor
R1-R3 - 1K ohm, 1/4w, 10% resistor
(The 48 diodes in the diode matrix are 1N914 signal diodes)
D/S1-D/S3 - Digitran Co., rotary encoding thumbwheel switches, decimal to binary coded decimal 8421, each unit is a four digit encoder.
Comparator
P1,3,5 - 100K ohm 1/8w, one turn potentiometer
P2,4,6 - 5K *
R1-R9 - 1K, 1/4w, 10%, resistor
Q1-Q3 - 2N2222 transistor
C1-C3 - 1nf cerm. cap.
(Photoresistor is non-critical component - may be replaced by any unit of same physical size--then adjust P1-P6 of comparator)
(Comparator Parts List continued)

IC1-IC3 - National Semiconductor LM311H comparator

**Master Sequencer**

IC1-IC3 - Texas Instr., SN7472N JK Flip-flop
R8,16,24 - 200 ohm, 1/4w, 10% resistor
R_x -(all other resistors are 1K ohm, 1/4w, 10%)
C1-C3 - 250 uf, 10vdc elec. cap.
Q2,5,8 - 2N2222 transistor
Q3,6,7 - 2N2646 unijunction transistor
P1,2,3 - 100K ohm, 1/8w, one turn potentiometer

**Miscellaneous**

All IC's are mounted in sockets: 14DIP, 16DIP, TO-5, TO-10
Power supply is intermittently decoupled by 0.1uf cer. cap.
Interconnections between boards are by way of plugs of assorted types.
Subunits are constructed of either printed circuits or conventional breadboard.

**INTERCONNECTIONS**

The subunit interconnections are in most cases denoted by the letter and color codes of the circuit diagrams. $V_{CC}$ always refers to 5 volts d.c. The numbers given on the syringe wiring diagram refer to the number code of the cable wires connecting the syringes to the main chassis.

The following is the letter code key used throughout the wiring diagrams:

- L-counter load input
- P-counter preset input
- R-refill of sequencer board
CSI-counter sequencer interface
S-sequencer
Strobe-Comparator Strobe Control

The board interconnection chart for the Master Sequencer is:

L1-CSI Preset 2
L2-CSI Preset 3
L3-CSI Preset 1
R3-S3 Refill
Q3-Strobe 3
CLK3-Q3 of CSI
P3-Panel D/R pb to ground
R2-S2 Refill
Q2-Strobe 2
CLK2-Q2 of CSI
P2-Panel D/R pb to ground
R1-S1 Refill
Q1-Strobe 1
CLK1-Q1 of CSI
P1-Panel D/R pb to ground

The board interconnection chart for the Sequencer is:

<table>
<thead>
<tr>
<th>Cable Wire#</th>
<th>Board Conn.#</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>(refill input)</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Gnd</td>
<td>6</td>
</tr>
<tr>
<td>120 vac supply</td>
<td>12</td>
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<td>11</td>
<td>13</td>
</tr>
<tr>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

(Cable #'s 10,13 to AC common)