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KINETICS OF THE METHYL IODIDE CATALYZED AND AUTOCATALYZED ARBUZOV REARRANGEMENT

by

BRIDGET A. MCCORTNEY

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

DOCTOR OF PHILOSOPHY

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May, 1986
Abstract

Rates for the two sequential steps of the Arbuzov rearrangement:\[\text{Me} \rightarrow \text{Me}^{\text{Me}}\]
\[\text{ABPOMe} \rightarrow \text{ABP(O)Me}, \ A, B = \text{OMe, OMe; OMe, Ph; Ph, Ph; OMe, Et; and Et, Et were measured by conductivity. The concentration of the methoxyphosphonium iodide intermediates was determined from calibration curves relating conductivity to concentration for the analogous stable ethylphosphonium iodides. No significant contribution from the autocatalytic Arbuzov rearrangement:}\]
\[\text{ABPOMe} \rightarrow \text{ABP(O)Me, was observed for these reactions. For all cases except methyl diethylphosphinite (A = B = Et), the rate determining step is the alkylation of the trivalent phosphorus ester. Rates for the autocatalytic Arbuzov rearrangement of the same compounds were measured by}^{31}\text{P nmr. The substituent effect (}\rho_{\text{I}}\text{) for the reactions was determined by correlation of the kinetic data with the sum of the Taft inductive parameters (}\sigma_{\text{I}}\text{) of the substituents on phosphorus. The }\rho_{\text{I}}\text{ values for the two steps of the "textbook" Arbuzov rearrangement are -4.6 and 5.6 respectively. The }\rho_{\text{I}}\text{ for the autocatalytic Arbuzov rearrangement is 0.75.}]}
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To my parents, Barney and Mary Jane.
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Introduction

The Arbuzov reaction (often referred to as the Michaelis-Arbuzov reaction), equation 1.1, was first discovered in 1898 by Michaelis and Kaehne\textsuperscript{1}. The overall reaction consists of conversion of a trivalent phosphorus ester into a pentavalent phosphoryl compound with formation of a new phosphorus-carbon bond. An alkylating agent, usually an alkyl halide, is used to effect this transformation. The process is called "valency expansion", and results in the formation of a high energy (120-150 kcal/mole) P=O bond.\textsuperscript{2} The result is an estimated net gain in bond energy of the molecule of 32-65 kcal/mole.\textsuperscript{3} Scheme 1.1 (page 2) details the nomenclature of phosphorus compounds in the Arbuzov reaction.

A.E. Arbuzov studied the reaction in detail and in 1906 proposed the following two step mechanism involving a pentacoordinate phosphorane intermediate (equation 1.2).\textsuperscript{4}
Nomenclature of Phosphorus Compounds
Involved in the Arbuzov Reaction

\[(\text{MeO})_3\text{P} + \text{MeI} \rightarrow (\text{MeO})_3\text{P}^+\text{Me}^- \rightarrow (\text{MeO})_3\text{PMe} + \text{MeI}\]

trimethyl phosphite  \hspace{1cm} methyltrimethoxyphosphonium iodide  \hspace{1cm} dimethyl methylphosphonate

\[\text{MeI} \quad \text{PhP(OMe)}_2 \quad \text{MeI} \quad \text{O}\]

dimethyl phenylphosphonite \hspace{1cm} methyl methylphenylphosphinate

\[\text{MeI} \quad \text{Et}_2\text{POMe} \quad \text{MeI} \quad \text{O}\]

methyl diethylphosphinitite \hspace{1cm} diethylmethylphosphine oxide
Subsequent investigations have led to the conclusion that most Arbuzov reactions proceed through a mechanism consisting of two sequential $Sn2$ displacement reactions, equations 1.3 and 1.4. This mechanism is referred to as

\[ (\text{I}) \quad (\text{RO})_3\text{P}^- + \text{R'}\cdot\text{X} \rightarrow (\text{RO})_2\text{P}^+\text{R}^- + \text{X}^- \]

\[ (\text{II}) \]

\[ (\text{III}) \quad (\text{RO})_2\text{P}^-\text{O} + \text{R'}\cdot\text{X} \rightarrow (\text{RO})_2\text{P}=\text{O} + \text{RX} \]

the "textbook" mechanism to distinguish it from other more recently discovered mechanisms by which the Arbuzov reaction can occur. These mechanisms will be described later.

When $\text{R} = \text{R'}$, the reaction is simply a rearrangement of the reactant phosphorus ester in which the alkylating agent acts as a catalyst. When $\text{R}$ and $\text{R'}$ are different, complex product mixtures may result through the reaction of both $\text{RX}$ and $\text{R'X}$ with the phosphite. The product distribution will depend on the relative alkylating ability of $\text{RX}$ and $\text{R'X}$ and the rates of the two steps of the reaction.

The "textbook" mechanism differs from Arbuzov's originally proposed mechanism only in the nature of the intermediate, which is now thought to be a tetracoordinate phosphonium ion rather than a pentacovalent phosphorane. The existence of the intermediate as a phosphorane or a phosphonium salt was the subject of considerable controversy.\(^5,6\) \(^{31}\text{P}\) nmr spectroscopy proved to be a valuable tool in establishing the structure as a phosphonium
salt; the chemical shift of a phosphonium salt is far removed from that of a phosphorane in $^{31}$P nmr spectra. The observance of chemical shifts of intermediates in the correct range for phosphonium ions and their independence on the counterion $X^-$ has confirmed the intermediacy of phosphonium ions in Arbuzov reactions. It is now generally accepted that in reactions of phosphorus esters containing simple alkyl, aryl, alkoxy, aryloxy, and dialkylamino substituents the intermediate exists as a phosphonium ion. Phosphoranes, however, have been detected by $^{31}$P nmr as intermediates in the reactions of phosphorus esters containing very electronegative substituents for which the positively charged phosphonium structure would be highly destabilized (equation 1.5). Likewise,

$$\text{(1.5)} \quad \text{F} \quad \text{Cl} \quad \text{+ P(OMe)$_3$} \quad \rightarrow \quad \text{F} \quad \text{Cl} \quad \text{140°} \quad \text{F} \quad \text{Cl} \quad \text{P(OMe)$_2$}$$

phosphoranes have been seen in reactions of phosphorus esters that are part of a five-membered o-phenylene ring (equations 1.6 and 1.7). The stability of these

$$\text{(1.6)} \quad \text{Cl}_2 \quad \text{P-OEt} \quad \text{Cl} \quad \text{-85°} \quad \text{P-OEt} \quad \text{Cl} \quad \text{-40°} \quad \text{P-OEt} \quad \text{Cl}$$

$$\text{(1.7)} \quad \text{Et}_2\text{NCl} \quad \text{P-OEt} \quad \text{-50°} \quad \text{P-OEt} \quad \text{NET}_2$$
phosphoranes is attributed to a reduction in steric bulk when the ring substituents occupy apical and equatorial positions in the trigonal bipyramidal phosphorane. Direct dealkylation of the phosphorane intermediate has been ruled out in the case of equation 1.6 on the basis of stereochemical evidence; reaction of the (R)-2-octyl ester gives (S)-2-chlorooctane. The reaction is thought to proceed through the establishment of a fast equilibrium between the phosphorane and phosphonium ion which decomposes by SN2 dealkylation. The presence of both four and five coordinate intermediates has been observed in reaction 1.7 at -50 °C, while at higher temperatures (-15 °C) the peak due to the phosphorane disappears completely.

The isolation of numerous alkoxyphosphonium salts through the reaction of a phosphorus ester with an alkylation agent further supports their intermediacy in the Arbuzov reaction. Phosphonium salts have been isolated and characterized for reactions of triaryl phosphites with methyl iodide. Here the resistance of the phenyl group to nucleophilic attack allows isolation of the phosphonium salt. 1-norbornoxytriphenylphosphonium chloride and 1-[2.2.2]bicyclooctanoxytriphenylphosphonium chloride have also been obtained as a consequence of the resistance of a bridgehead atom to nucleophilic attack. There is even a report of the isolation of a short-lived phosphonium salt from the reaction of methyl diethylphosphinite with methyl iodide. In general, only the more sterically hindered
alkoxyphosphonium halides (compound II, page 3, where R = neopentyl\textsuperscript{18}, isobutyl\textsuperscript{19}, isopropyl\textsuperscript{20}, and 2,2,2-triphenylethyl\textsuperscript{21}) can be isolated and stored at room temperature. In addition, unhindered alkoxyphosphonium salts where the anion X is non-nucleophilic (trifluoromethanesulfonate\textsuperscript{22}, tetrafluoroborate\textsuperscript{23}, tetr phenylborate\textsuperscript{24}, and hexachloroantimonate\textsuperscript{25}) have also been prepared. In these cases, it is the very slow rate of reaction 1.4 which stabilizes the salt.

There is ample evidence to support an S\textsubscript{n}2 reaction for the first step of the "textbook" mechanism. Trivalent phosphorus compounds are known to be good nucleophiles\textsuperscript{26} and the analogous reaction of trialkylphosphines with alkyl halides has been determined to follow an S\textsubscript{n}2 mechanism\textsuperscript{27,28}. The usual order of reactivity of a phosphorus ester with a series of halides is acyl > primary alkyl > secondary alkyl and iodide > bromide > chloride\textsuperscript{29}; which is the order typically observed in S\textsubscript{n}2 displacement reactions\textsuperscript{30}.

Kosolapoff's semi-quantitative study of the reaction between triethyl phosphite and \textit{n}-hexyl and \textit{n}-butyl bromide supports a two-step reaction mechanism\textsuperscript{31}. The ethyl bromide was removed upon formation to prevent its reaction with triethyl phosphite. A sigmoidal curve was obtained for the rate of ethyl bromide formation with time, which in the author's opinion indicates that an induction period corresponding to accumulation of the phosphonium intermediate is necessary after which formation of ethyl
bromide by dealkylation of the intermediate is rapid. In 1964, Aksnes and Aksnes confirmed the rate determining formation of the intermediate in their study of the reactions of triethyl phosphite, diethyl phenylphosphonite, and ethyl diphenylphosphinito with ethyl iodide. They found that the rate of formation of product is proportional to the ethyl iodide concentration which remains essentially constant throughout the reaction. The activation energies of the reactions were found to increase with increasing number of ethoxy substituents on phosphorus. This indicates that the greater electron withdrawing effect of the ethoxy group decreases the rate of reaction of the phosphorus esters with ethyl iodide. The same effect was observed in reactions of substituted dimethyl arylphosphonites with methyl iodide in which electron attracting substituents on the phenyl ring result in a lower rate of reaction.

The second step of the Arbuzov reaction is also considered to be an $S_{N}2$ displacement of $R$ from an alkoxy group of (II) by the anion $X$. Supporting evidence lies in the decomposition of methyltrineopentoxyphosphonium iodide in CHCl$_3$ which gives neopentyl iodide with no rearrangement product detected. In addition, reaction of tri-((S)-2-octyl) phosphite with ethyl iodide results in stereospecific formation of (R)-2-octyl iodide and di((S)-2-octyl) ethylphosphonate through the intermediate ethyltri((S)-2-octyl)phosphonium ion (equations 1.10 and 1.11), showing that inversion of configuration occurs in this reaction.
(1.10) \((\text{C}_6\text{H}_{13}-\text{C}-\text{O})_3\text{P} + \text{EtI} \rightarrow (\text{C}_6\text{H}_{13}-\text{C}-\text{O})_3\text{P}^+\text{Et} + \text{I}^-\)  
\((\text{S})\) \((\text{S})\) 

(1.1) \((\text{C}_6\text{H}_{13}-\text{C}-\text{O})_3\text{P}^+\text{Et} + \text{I}^- \rightarrow (\text{C}_6\text{H}_{13}-\text{C}-\text{O})_2\text{P}^+\text{Et} + \text{I}^-\text{C}^-\text{C}_6\text{H}_{13}\)  
\((\text{S})\) \((\text{S})\) \((\text{R})\) 

The overall reaction is also stereospecific as confirmed by the conversion of cis-2-methoxy-4-methyl-1,3,2-dioxaphosphorinane (IV) to trans-phosphonate (V) by reaction with methyl iodide, and conversion of the trans-methyl ester (VI) into the cis-phosphonate (VII) as shown in equations 1.12 and 1.13.\(^{35}\) Earlier reports that the reactions of the ethyl and isopropyl esters were non-stereospecific (explained by the formation of a pentacovalent phosphorane intermediate which undergoes pseudorotation\(^{26}\)) have been attributed to the presence of acid impurities which cause rapid isomerization of the cis phosphite to the trans phosphite.\(^{35}\)
Nearly all rate constants for the second step of the "textbook" mechanism have been obtained only for "stable" alkoxyphosphonium salts. These have naturally been restricted to compounds that can be isolated at convenient temperatures. The decomposition of several phosphonium salts containing neopentoxy\(^{37}\), isopropoxy\(^{38}\), and isobutoxy\(^{39}\), groups have been measured in both polar and nonpolar solvents. The kinetic order of the reaction was found to be dependent on the solvent for the decomposition of \((\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3\text{CH}_2\text{O})\text{P}^+\text{(NMMe}_3\text{)}\text{Cl}^-\) at 45.0 °C, monitored by titration of the unreacted Cl\(^-\).\(^{40}\) The reaction is second order when run in MeOH, but between first and second in DMF, acetone, and methyl ethyl ketone. The order of the reaction also depends on the concentration of the phosphonium ion; for example, Nesterov and Aleksandrova found that decomposition of EtP\(^+\)\((\text{OisoBu})_2\text{Me}I^-\) (followed by conductivity) is second order in CH\(_3\)CN at 20 °C for phosphonium salt concentrations less than 0.01 molar and first order for higher concentrations.\(^{39}\) This indicates that in very polar solvents at low phosphonium ion concentrations, attack of the alkoxyphosphonium ion by \(X^-\) occurs between dissociated ions; but in less polar solvents and in polar solvents at high phosphonium ion concentrations, some reaction also occurs within undissociated ion pairs.

The Lee reaction (equations 1.14 - 1.16) is a general method for the synthesis of alkyl chlorides from alcohols
(1.14) $\text{Ph}_3\text{P} + \text{CCl}_4 \rightarrow \text{Ph}_3\text{P}^+\text{Cl} + \text{CCl}_3^-$

(1.15) $\text{Ph}_3\text{P}^+\text{Cl} + \text{ROH} + \text{CCl}_3^- \rightarrow \text{Ph}_3\text{P}^+\text{OR} + \text{Cl}^- + \text{HCCl}_3$

(1.16) $\text{Ph}_3\text{P}^+\text{OR} + \text{Cl}^- \rightarrow \text{Ph}_3\text{P}=\text{O} + \text{RCl}$

which proceeds through an intermediate alkoxyphosphonium halide that decomposes in manner equivalent to the second step of the Arbuzov reaction. For reactions where $R =$ secondary alkyl or neopentyl, the rate determining step is attack by chloride on the alkoxytriphenylphosphonium ion in equation (1.16). The decomposition of alkoxyphosphonium ions in the Lee reaction has also been found to be first order in nonpolar solvents (CDCl$_3$ and CCl$_4$) and second order in the polar solvent CH$_3$CN. Studies of the Lee reaction have yielded valuable information on the mechanism of decomposition of alkoxyphosphonium ions.

The observed first order reaction of alkoxyphosphonium halides can be representative of four different mechanisms: (1) rate determining reaction within an ion pair, (2) rate determining dissociation of the ion pair followed by rapid reaction of the free ions, (3) formation of a small steady-state concentration of free ions which react, or (4) a concerted pericyclic mechanism. The $\sigma$ 2s + $\sigma$ 2a thermal pericyclic mechanism proposed by Knaggs, Davies and Aneja can be excluded on the basis of the experimentally observed solvent dependence on the order of the reaction. This solvent dependence is not expected for a concerted process. This mechanism also includes a phosphorane intermediate as
the reactive species which has not been detected. The failure of external nucleophiles to react with the phosphonium ions has been observed by Weiss and Snyder\textsuperscript{43} who found that reaction of 2-phenylethanol, carbon tetrachloride, triphenylphosphine and sodium cyanide in dimethylsulfoxide yielded only 2-phenylethyl chloride and no 2-phenylethyl cyanide. The rate determining reaction, therefore, cannot be between dissociated ions, but must occur within an ion pair. This result eliminates mechanisms (2) and (3) above.

A valid mechanism must also include back side attack of $X^-$ on the carbon $\alpha$ to the oxygen to account for the observed stereochemistry (inversion\textsuperscript{43}) and the slow rate of reaction of neopentoxyphosphonium ions. Molecular models show that the neopentyl system is only slightly hindered to front side attack but is highly hindered to back side attack.\textsuperscript{42} Two mechanisms have been proposed that account for the available data. Franzus proposed an ion cluster mechanism (equation 1.17) for the decomposition of neopentoxytriphenyl-

\[
(1.17) \quad \text{Cl}^- \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \begin{array}{c} \text{Ph} \\ \text{Ph} \end{array} \begin{array}{c} \text{C(CH}_3)_3 \\ \text{O} \end{array} \begin{array}{c} \text{H} \\ \text{H} \end{array} \rightarrow \text{Ph}_3\text{P}=\text{O} + \begin{array}{c} \text{(H}_3\text{C})_3\text{C} \\ \text{Cl} \end{array}
\]

phosphonium chlorides in the Lee reaction.\textsuperscript{42} In this mechanism, first order decomposition of a cluster of intimate ion pairs in two and/or three dimensions is stabilized by virtue of a postively charged phosphorus in
one ion pair adjacent to a negatively charged chloride from another ion pair. Thus, the collapse is from the backside of the α carbon to form the inverted product. From studies on the decomposition of neopentoxyphosphonium halides, Hudson has proposed rate determining collapse to products within an undissociated ion pair which undergoes a small change in reorientation from association of the halide with the phosphorus center to association of the halide with Cα in the transition state (equation 1.18).37

\[
\begin{array}{c}
\text{RO-} \quad \text{O-} \quad \text{R} \\
\text{RO-} \quad \text{P}^+ \quad \text{...} \quad \text{X}^- \\
\text{R'}
\end{array}
\rightarrow
\begin{array}{c}
\text{RO} \\
\text{RO-} \quad \text{O} \quad \text{...} \quad \text{R} \quad \text{...} \quad \text{X}^{5+} \\
\text{RO} \\
\text{RO-} \quad \text{P}^+ \quad \text{...} \quad \text{R'}
\end{array}
\]

(1.18)

The available stereochemical, energetic, and isotopic data are consistent with both of the above mechanisms. The enthalpy of activation (ΔH‡) for reactions of this type has been determined to be approximately 25 – 30 kcal/mole37,42, a value which is essentially equal to the 26 kcal/mole obtained for the Sx2 reaction of neopentylbromide with ethoxide.45 Values of the entropy of activation37,42 (ΔS‡) are very close to zero which is consistent with the small amount of reorganization necessary in the transition states for both mechanisms. It has been suggested, however, that the ion cluster mechanism can be distinguished on kinetic grounds.46 The order of the reaction should change from first to second as the phosphonium salt concentration decreases and formation of the ion clusters becomes rate determining. However, none of the kinetic
studies$^{37,41,42,44}$ report any deviation from first order behavior. Thus, Hudson's mechanism, which is expected to follow first order kinetics throughout the reaction, appears more reasonable.

It is uncertain that these results can be extrapolated to other systems. Factors other than inductive and resonance effects may be significant in determining the reactivity of phosphonium ions under these conditions. For example, if Hudson's mechanism is correct, the ability of a given nucleophile to "reorient" will be important in determining the activation barrier for reaction. It is possible that "soft" nucleophiles will react unnaturally slowly (due to their preference for association with the "soft" phosphorus center) and "hard" nucleophiles (which prefer association with the "hard" carbon center) will react unnaturally fast. There is also the possibility of substantial steric influence on the rate of the reaction due to the large bulk of the nonreacting neopentoxy phosphorus substituents. A further complication is that fission of the R-0 bond may occur in advance of attack by the external nucleophile (Sn1 mechanism) in the decomposition of some alkoxyphosphonium ions. This is evidenced by the formation of some rearrangement product (tert-pentyl halide) in the reactions of neopentyl diphenylphosphinites and dineopentyl phenylphosphononitites with alkyl halides.$^{47}$ The reaction of triphenylphosphine, carbon tetrachloride, and (R)-(+)2-octanol in CH$_3$CN (Lee reaction) gave 78% racemic 2-
chloro-octane.\textsuperscript{41} These results indicate that the Sn1 fission is encouraged by electron attracting substituents (which destabilize the phosphonium ion) and highly polar solvents (which can solvate the resulting carbenium ion R\textsuperscript{+}). It is certainly more desirable to study the decomposition of phosphonium ions under second order conditions where the above complications and mechanistic uncertainties can be avoided.

In 1951, Rumpf proposed that the Arbuzov reaction may also proceed through an autocatalytic mechanism (equation 1.19 and 1.20).\textsuperscript{48} This suggestion was experimentally
\begin{equation}
(1.19) \quad (\text{RO})_3\text{P} + \text{R}'\text{X} \rightarrow (\text{RO})_3\text{P}^+\text{R}' + \text{X}^- \\
(\text{VIII}) \quad (\text{IX})
\end{equation}
confirmed by Nesterov and Kessel who found that the reaction of methyltrimethoxyphosphonium tetrafluoroborate and trimethyl phosphite gave dimethyl methylphosphonate from which the phosphonium ion was recovered quantitatively (equation 1.21).\textsuperscript{49} A similar reaction was observed for triethyl phosphite and ethyltrithoxyphosphonium tetrafluoroborate.\textsuperscript{49}
\begin{equation}
(1.20) \quad \text{RO}_3\text{P}^- + \text{RO} + \text{R}'\text{O}_2\text{P}^- \rightarrow \text{RO}^+\text{R} + \text{RO} + \text{R}'\text{P}=\text{O} \\
(\text{VIII}) \quad (\text{IX}) \quad (\text{X}) \quad (\text{XI})
\end{equation}
\begin{equation}
(1.21) \quad \text{MeP}^+(\text{OMe})_3\text{BF}_4^- + (\text{MeO})_3\text{P} \rightarrow (\text{MeO})_2\text{PMe} + \text{MeP}^+(\text{OMe})_3
\end{equation}
Lewis and Colle also observed the rearrangement of trimethyl phosphite to dimethyl methylphosphonate "catalyzed" by methyltrimethoxyphosphonium trifluoromethane-sulfonate (equation 1.21 substituting OTf- for BF4-), and they measured the enthalpy of reaction to be -24.2 kcal/mole.50

One might expect that the extent of autocatalysis can be determined from the product mixture resulting when R and R' are different. The salt produced (X) by autocatalysis will give rise to a different phosphonate, (RO)2P(O)R, than the "textbook" mechanism (XI). However, the reaction of (X) with the nucleophile X- will lead to the formation of RX which can produce (RO)2P(O)R via the "textbook" route. The rate of the autocatalytic Arbuzov reaction can thus most easily be determined through the deviation of the reaction kinetics from "normal" behavior, or under conditions in which this is the only possible pathway for reaction of the phosphonium salt (as in equation 1.21).

Hamp and Lewis studied the Arbuzov rearrangement of phosphorus methyl esters with methyl iodide, dimethyl-sulfate, and methyl trifluoromethanesulfonate using 31P nmr.51 They found that in the reactions with methyl iodide no significant autocatalysis occurred, while for reactions with methyl trifluoromethanesulfonate the only product-forming reaction was autocatalysis. For reactions involving dimethylsulfate, there was a contribution from both the "textbook" mechanism and autocatalysis. Thus, it appears
that the autocatalytic Arbuzov reaction becomes important when the counterion X⁻ is weakly nucleophilic and when the alkylating agent is strong, resulting in the accumulation of high phosphonium ion concentrations. The extent of autocatalysis observed in the Arbuzov rearrangement is a result of a combination of these two factors.

In addition to the "textbook" and autocatalytic mechanisms, the Arbuzov reaction can occur by various other routes. There are several examples of free radical Arbuzov reactions in which an alkyl or aryl radical reacts with a trivalent phosphorus ester (equation 1.22).\(^5\) This reaction is catalytic when \(R = R'\). An anionic Arbuzov reaction has

\[
(1.22) \quad R'\cdot + P(OR)_3 \rightarrow R'\cdot P(OR)_3 \rightarrow (RO)\_2P=O + R'\cdot
\]

also very recently been seen\(^5\) (equation 1.23) which is the autocatalytic equivalent of the well-known reaction of

\[
(1.23) \quad \text{Ph}_2P=\text{O} + \text{Ph}_2\text{POMe} \rightarrow \text{Ph}_2P(\text{O})\text{Me} + \text{Ph}_2P=\text{O}
\]

phosphonate anions with alkyl halides (equation 1.24).\(^5\)

\[
(1.24) \quad (RO)\_2P=\text{O} \ Na^+ + R'X \rightarrow R'P(\text{O})(OR)\_2 + NaX
\]

Arbuzov reactions with aryl iodides and phosphites (which cannot undergo S\(_n\)2 reaction in the usual manner) to give dialkyl arylphosphonates have been observed in the
presence of \( \text{NiCl}_2 \) and \( \text{CuCl}_2 \), presumably through catalytic activation of the aryl-iodide bond. Arylphosphonates are also formed from photolysis of aryl iodides and phosphites via a free radical reaction (equation 1.22).\(^{57}\)

Arbuzov-like dealkylation reactions of transition metal phosphite complexes are quite common, occurring in complexes of cobalt, iron, nickel, rhenium, manganese, and tungsten.\(^{58}\) The reaction is not as predictable as the classical Arbuzov reaction, occurring not at all in some complexes and rapidly at room temperatures in others. In general, the organo-metallic dealkylation is \(10^4 - 10^6\) times faster than the equivalent Arbuzov reaction.\(^{58}\) The mechanism proposed for the reaction of \(\text{CpCo(dppe)I}^+\) and \(\text{P(OMe)_3}\) is shown in equation 1.25.

\[
\text{(1.25)} \quad \text{Cp} \quad \text{Co} \quad \text{P} \quad \text{I} \quad + \text{P(OMe)_3} \quad \text{Cp} \quad \text{Cp} \quad \text{P} \quad \text{P} \quad \text{OMe} \quad + \text{I}^{-} \quad \text{Cp} \quad \text{Cp} \quad \text{P} \quad \text{P} \quad \text{OMe} \quad + \text{MeI}
\]

Arbuzov reactions have also been found to occur for reactions of trivalent phosphorus esters with compounds other than common alkylating agents. For example, trialkyl phosphites react with carbonyl-stabilized ylides in what is called a nonclassical Arbuzov rearrangement (equation 1.26 - 1.29).\(^{59}\) A reaction of trialkyl phosphites with \(N\)-acyl-

\[
\text{(1.26)} \quad \text{S-Ph} \quad + \quad \text{P(OR)_3} \quad \text{S-Ph} \quad + \quad \text{R'P^+(OR)_3}
\]
aziridines is thought to proceed through an Arbuzov-like mechanism in which dealkylation takes place through a six-center transition state (equation 1.30).\(^{60}\)

Alkoxyphosphonium ions which are stabilized by a non-nucleophilic counterion are susceptible to attack by other nucleophiles, as seen in the autocatalytic Arbuzov reaction. This property has been exploited in their use as general purpose alkylating agents.\(^{61,62}\) Alkoxyphosphonium ions have been shown to react with a wide variety of nucleophiles including alkyl alcohols, thiols, acids, and amines.\(^{62}\)

The Arbuzov reaction has found widespread use in the synthesis of phosphonate and phosphinate esters and tertiary phosphine oxides. The reaction takes place for a wide variety of substituents on both phosphorus and the alkyl halide. More recent developments include its use in the
synthesis of derivatives of biologically important compounds. Amino-phosphonic analogs of naturally occurring amino acids (XII) are being incorporated into peptides which show antibacterial activity, while phosphonic acid analogs of nucleotides (XIII) are being used to investigate the mechanism of action of natural nucleotides.

![Chemical structures](image)

(XII)  
(XIII)

The Arbuzov reaction is also used to synthesize phosphonates added to polymers and polymers containing phosphonate groups which have been found to exhibit fire-retardant properties, and are used as fireproofing agents for plastics and textiles.

Despite its widespread use and previous investigations, there exists little quantitative information on the Arbuzov reaction. It is known that electron releasing substituents on phosphorus accelerate the first step of the "textbook" mechanism and retard the second. However, the relative importance of these effects is as yet unknown. A thorough understanding of both steps of the Arbuzov reaction is critical to its successful application in synthetic
chemistry. This study was undertaken in an effort to uncover the dominating substituent effect on the Arbuzov rearrangement and to develop a precise experimental method whereby rates for both steps of the "textbook" mechanism could be obtained. The $^{31}\text{P}$ nmr method previously used in this laboratory$^{46}$ did not afford the precision necessary for such a study; we therefore chose electrical conductivity as the method for following the reaction. To insure $\text{S}_\text{N}2$ reactions, the isomerization of phosphorus methyl esters by methyl iodide was studied. The problems associated with first order decomposition were avoided through the use of a solvent with a very high dielectric constant, propylene carbonate (XIV) In this manner, complete dissociation of

\[
\text{(XIV)}
\]

the phosphonium intermediates was insured. In addition, rate constants for the autocatalytic Arbuzov rearrangement were measured by $^{31}\text{P}$ nmr for the reaction of methoxyphosphonium triflates with phosphorus methyl esters.
Results

The Arbuzov reactions of trivalent phosphorus methyl esters with methyl iodide have been shown to proceed solely by the "textbook" mechanism (equations 2.1 and 2.2).\textsuperscript{51} The autocatalytic reaction (equation 2.3) does not contribute significantly due to the high nucleophilicity of the iodide anion\textsuperscript{67} ($k_2 \gg k_3$).

\begin{align*}
(2.1) \quad ABPOMe + MeI & \xrightarrow{k_1} ABP^+\text{(OMe)}Me + I^- \\
(2.2) \quad ABP^+\text{(OMe)}Me + I^- & \xrightarrow{k_2} ABP\text{(OMe)} + MeI \\
(2.3) \quad ABP^+\text{(OMe)}Me + ABP\text{(OMe)} & \xrightarrow{k_3} AP\text{(OMe)} + ABP^+\text{(OMe)}Me
\end{align*}

The differential rate equations for the "textbook" mechanism are given in equations 2.4 through 2.7.

\begin{align*}
(2.4) \quad & d[ABPOMe]/dt = -k_1[ABPOMe][MeI] \\
(2.5) \quad & d[MeI]/dt = -k_1[ABPOMe][MeI] + k_2[ABP^+\text{(OMe)}Me][I^-] \\
(2.6) \quad & d[ABP^+\text{(OMe)}Me]/dt = k_1[ABPOMe][MeI] - k_2[ABP^+\text{(OMe)}Me][I^-] = -d[MeI]/dt \\
(2.7) \quad & d[ABP\text{(OMe)}]/dt = k_2[ABP^+\text{(OMe)}Me][I^-]
\end{align*}
In equations 2.5 - 2.7, we assume that the intermediate phosphonium ion is completely dissociated under the conditions of the reaction. The solvent used in the kinetic studies, propylene carbonate (propanediol-1,2-carbonate), is a polar aprotic solvent with a very high dielectric constant (64.4 at 25 °C compared to 78.5 for H₂O⁶⁹, 46.7 for CH₃SOCH₃⁶⁹, 37.5 for CH₃CN⁶⁹, and 20.7 for CH₃COCH₃⁶⁹), which should ensure complete dissociation of the phosphonium ions at the concentrations used. The rate constant k₂ is thus the second order rate constant for decay of the phosphonium ion. When the conductivity of an Arbuzov reaction is measured as a function of time, data such as those shown in figure 2.1 are obtained. The conductivity of the reaction solution rises until a maximum is reached (corresponding to a steady state of the intermediate phosphonium ion concentration) and decreases until all of the phosphorus ester is converted into the Arbuzov product, ABP(O)Me. The observed conductivity is proportional to the concentration of the intermediate phosphonium ion, but the concentration does not follow a simple kinetic law. In cases such as this, the easiest method to determine the rate constants for the individual steps of the reaction is to integrate numerically the differential rate equations describing the reaction. In order to derive the rate constants for the two steps of the "textbook" mechanism from those data, it is clear that we first need to determine the relationship between concentration and conductivity for the
Figure 2.1 Specific conductivity as a function of time for the reaction:

\[
\text{MeI} \rightarrow \text{Ph}_2\text{P(OMe)}
\]

in propylene carbonate at 25.0 °C

\([\text{Ph}_2\text{POMe}]_0 = 0.02255 \text{ molar}\)

\([\text{MeI}]_0 = 0.07500 \text{ molar}\)
intermediate phosphonium ion. However, the intermediates of the reactions we are interested in are unstable under the conditions of the reaction (the decomposition of methoxyphosphonium iodides with unhindered alkyl and phenyl substituents is known to be fast\textsuperscript{51}). Therefore, it is not possible to isolate the salts and directly measure their conductivity as a function of concentration. It was thought, however, that the analogous ethylphosphonium iodides, ABP\textsuperscript{+}(CH\textsubscript{2}CH\textsubscript{3})CH\textsubscript{3} could be used as models for the unstable methoxyphosphonium iodides, ABP\textsuperscript{+}(OCH\textsubscript{3})CH\textsubscript{3}.

Ethylphosphonium iodides are stable to attack by nucleophiles since lack an alkoxy group attached to phosphorus. The conductivity of an ionic species in solution is proportional to the charge on the ion and inversely proportional to its size and the viscosity of the solvent.\textsuperscript{70} Therefore, in the comparison of ethyl- and methoxyphosphonium ions, we need only consider the possible difference in their sizes. The substitution of a methylene group (–CH\textsubscript{2}–) for an oxygen (–O–) should have very little effect on the size and hence the conductivity of the phosphonium ions. The comparison of 2-aminoethylphosphate (XV) and 2-aminoethylphosphonic acid (XVI) provides support for this hypothesis. From crystallographic data on the two

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{CH}_2\overset{\text{a}}{P}\overset{\text{b}}{O}\overset{\text{O}}{H} & \quad \text{(XV)} \\
\text{H}_2\text{NCH}_2\overset{\text{a}'}{\text{CH}_2}\overset{\text{b}'}{P}\overset{\text{O}}{O}\overset{\text{H}}{H} & \quad \text{(XVI)}
\end{align*}
\]
compounds\textsuperscript{71,72}, it has been calculated\textsuperscript{64} that a variation of only 0.8\% in the distance between a—b and a'—b' exists (the phosphonic acid being greater). This similarity in size and shape has been exploited in the widespread use of phosphonic acid analogs of biological phosphates as metabolic regulators or perturbators.\textsuperscript{64} For example, (XVII) has been used as an analog of (XVIII) due to the very similar bond angles and lengths (the importance of precise size and shape relationships for binding and/or interaction sites in biological systems is well known\textsuperscript{73}).

The ethylphosphonium iodides were therefore expected to have the same concentration dependence of conductivity as the corresponding methoxyphosphonium iodides. This hypothesis was tested by synthesizing stable methoxyphosphonium trifluoromethanesulfonates (triflates) and ethylphosphonium triflates and comparing their dependence of the electrical conductivity on concentration. The specific conductivity was plotted as a linear function of concentration for the phosphonium triflate salts. Although
these are not rigorously proportional\textsuperscript{74}, this relationship has been frequently used in conductivity studies of phosphonium ions\textsuperscript{38,39,75}. The validity of this approximation in our studies will be discussed later in this section. We found that, within experimental error, solutions of methoxyphosphonium triflates have the same conductivity as solutions of ethylphosphonium triflates of equal concentration. The relationship between conductivity and concentration needed to analyze the experimental data can thus easily be obtained from ethylphosphonium iodides. Those data are reported in table 2.1 along with the conductivity data for methoxy- and ethylphosphonium triflates. For all of the phosphonium salts studied, very good linear plots were obtained ($r > 0.99$); in every case, the calculated intercept at zero concentration is small (ranging from $7.01 \times 10^{-7}$ - $5.5 \times 10^{-6}$). This insures that there is no significant ion pairing or phosphorane formation at the concentrations used. In fact, our experimental data fit a linear relationship better than the generally accepted Kohlrausch equation (2.8).\textsuperscript{74} $\kappa$ is the specific

\begin{equation}
(2.8) \quad (1000 \kappa) / c = \Lambda_m = \Lambda_m^0 - Kc^{1/2}
\end{equation}

conductivity, $c$ is the concentration of the ionic species, $\Lambda_m$ is the equivalent molar conductivity, $\Lambda_m^0$ is the limiting equivalent molar conductivity (equivalent molar conductivity at infinite dilution), and $K$ is a constant for a given
Table 2.1 Concentration dependence of the conductivity for the salts ABCP'Me X⁻ in propylene carbonate at 25.0 °C

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>X</th>
<th>Specific Conductivity/M (mho cm⁻¹)ᵃ</th>
<th>rᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>OMe</td>
<td>OTf</td>
<td>0.0229 ± 0.0012</td>
<td>0.9931</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Et</td>
<td>OTf</td>
<td>0.0238 ± 0.0001</td>
<td>0.9999</td>
</tr>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>Ph</td>
<td>OTf</td>
<td>0.0248 ± 0.0003</td>
<td>0.9998</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Ph</td>
<td>OTf</td>
<td>0.0241 ± 0.0003</td>
<td>0.9997</td>
</tr>
<tr>
<td>OMe</td>
<td>Ph</td>
<td>Ph</td>
<td>OTf</td>
<td>0.0244 ± 0.0005</td>
<td>0.9990</td>
</tr>
<tr>
<td>Et</td>
<td>Ph</td>
<td>Ph</td>
<td>OTf</td>
<td>0.0237 ± 0.0005</td>
<td>0.9995</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Et</td>
<td>I</td>
<td>0.0296 ± 0.0002</td>
<td>0.9999</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>Ph</td>
<td>I</td>
<td>0.0248 ± 0.0003</td>
<td>0.9997</td>
</tr>
<tr>
<td>Et</td>
<td>Ph</td>
<td>Ph</td>
<td>I</td>
<td>0.0256 ± 0.0003</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

ᵃ. Values reported are the slope ± S.D. of the specific conductivity vs. concentration plot.
ᵇ. Values reported are the correlation coefficient of the specific conductivity vs. concentration plot.
electrolyte. When $\Lambda_m^O$ is plotted vs. $c^{1/2}$ for our ethyl- and methoxyphosphonium salts, the correlation coefficients range from 0.83 to 0.99. Table 2.2 reports the limiting molar conductivities ($\Lambda_m^O$) of our salts determined in this manner. For comparison, values of $\Lambda_m^O$ for some phosphonium salts obtained by other workers are also listed along with those for some known strong electrolytes. The similarity of the $\Lambda_m^O$ values of the strong electrolytes (Me$_4$N$^+$I$^-$ and nBu$_4$N$^+$I$^-$) to those of our phosphonium ions reveals that the phosphonium iodides and triflates are also strong electrolytes in propylene carbonate as we had expected.

The validity of our approximation of a linear dependence of conductivity on concentration can be seen by comparing the specific conductivity vs. concentration plot for our linear relationship to that of the Kohlrausch equation (2.8) for each ethylphosphonium iodide studied. The plots obtained are shown in figures 2.2 -2.4. It is clear that in the concentration range used for the conductivity studies (salt concentration < 0.01M), the two relationships give virtually equal values for the concentration of salt when specific conductivity is measured. Thus, no accuracy in the concentration determination is lost by using this approximation; however, the calculations involved in the data analysis are greatly simplified. Figure 2.5 is an example of a plot of
Table 2.2 Limiting molar conductivities of some salts.

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\Lambda_m^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{MeO})_3\text{P}^+\text{Me} \quad \text{OTf}^-$</td>
<td>$33.1 \pm 2.2^b$</td>
</tr>
<tr>
<td>$(\text{MeO})_2\text{P}^+\text{PhMe} \quad \text{OTf}^-$</td>
<td>$27.7 \pm 0.6^b$</td>
</tr>
<tr>
<td>$(\text{MeO})\text{P}^+\text{Ph}_2\text{Me} \quad \text{OTf}^-$</td>
<td>$32.1 \pm 0.7^b$</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}^+\text{Me} \quad \text{OTf}^-$</td>
<td>$24.8 \pm 0.4^b$</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}^+\text{PhMe} \quad \text{OTf}^-$</td>
<td>$28.6 \pm 0.2^b$</td>
</tr>
<tr>
<td>$\text{EtP}^+\text{Ph}_2\text{Me} \quad \text{OTf}^-$</td>
<td>$29.4 \pm 0.3^b$</td>
</tr>
<tr>
<td>$(\text{PhO})_3\text{P}^+\text{Me} \quad \text{OTf}^-$</td>
<td>$22.1 (156)^c,f$</td>
</tr>
<tr>
<td>$(\text{PhO})_2\text{P}^+\text{PhMe} \quad \text{OTf}^-$</td>
<td>$23.8 (168) ^c,f$</td>
</tr>
<tr>
<td>$\text{PhOP}^+\text{Ph}_2\text{Me} \quad \text{OTf}^-$</td>
<td>$22.0 (155)^c,f$</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}^+\text{Me} \quad \text{I}^-$</td>
<td>$31.0 \pm 0.4^b$</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}^+\text{PhMe} \quad \text{I}^-$</td>
<td>$28.9 \pm 0.1^b$</td>
</tr>
<tr>
<td>$\text{EtP}^+\text{Ph}_2\text{Me} \quad \text{I}^-$</td>
<td>$31.6 \pm 0.5^b$</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}^+\text{Me} \quad \text{I}^-$</td>
<td>$20.6 (145)^d,f$</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}^+\text{Me}_2 \quad \text{I}^-$</td>
<td>$25.4 (179)^d,f$</td>
</tr>
<tr>
<td>$\text{Me}_4\text{N} \quad \text{I}^-$</td>
<td>$32.95^e$</td>
</tr>
<tr>
<td>$\text{nBu}_4\text{N} \quad \text{I}^-$</td>
<td>$27.33^e$</td>
</tr>
</tbody>
</table>

a. Values reported are for solutions of the salt in propylene carbonate at 25.0 °C unless otherwise noted.
b. Values reported are the slope ± S.D. of equivalent molar conductivity vs (concentration)$^{1/2}$ plot.
c. Reference 75.
d. Reference 76.
e. Reference 77.
f. Parenthetical value represents the limiting molar conductivity of the salt in CH$_3$CN which is divided by 7.05 (viscosity of propylene carbonate/viscosity of CH$_3$CN at 25 °C) to obtain the tabulated value. The viscosity of propylene carbonate is 2.53 cP from reference 68; the viscosity of CH$_3$CN is 0.359 cP from reference 78.
Figure 2.2 Specific conductivity as a function of concentration for $\text{Et}_3\text{P}^+\text{Me I}^-$ in propylene carbonate at 25.0 °C. Comparison of the linear and Kohlrausch equations.

Kohlrausch equation: $\kappa = (31.0(c) - 15.1(c)^{3/2})/1000$

linear equation: $\kappa = (29.6(c) + 0.000701)/1000$
Figure 2.3 Specific conductivity as a function of concentration for Et$_2$P$^+$PhMe I$^-$ in propylene carbonate at 25.0 °C. Comparison of linear and Kohlrausch equations.

Kohlrausch equation: $\kappa = (28.9(c) - 39.7(c)^{3/2})/1000$

linear equation: $\kappa = (24.8(c) + 0.00329)/1000$
Figure 2.4 Specific conductivity as a function of concentration for EtP²⁺Ph₂Me I⁻ in propylene carbonate at 25.0 °C. Comparison of linear and Kohlrausch equations.

Kohlrausch equation: \( \kappa = \frac{(31.1c - 53.1c^{3/2})}{1000} \)

Linear equation: \( \kappa = \frac{(25.6c + 0.00397)}{1000} \)
conductivity as a function of concentration for an ethylphosphonium iodide (methyltriethylphosphonium iodide).

From the concentration vs. time data for the similar ethylphosphonium iodide, the experimental conductivity vs. time data are converted into concentration vs. time data. Table 2.3 lists the Arbuzov reactions studied, their methoxyphosphonium iodide intermediates, and the ethylphosphonium iodide used to determine the concentration of the intermediate for that reaction. In all experiments, no phosphonium salt remained at the end of the reaction. Thus, \((k_2<<k_1)\) and the reverse of reaction (2.2) can be neglected. Alkylation of trivalent phosphorus compounds (reaction 2.1) is also known to be virtually irreversible \((k_1 >> k_1)\).\(^{28}\) The rate constants for the two steps of the "textbook" mechanism are obtained from direct numerical integration of the differential rate laws using a program developed earlier in this laboratory by Lewis and Hamp.\(^{46}\) Figure 2.6 shows an example of the fit obtained from this program to a set of experimental concentration vs. time data. Additional kinetic data are reported in Appendix I.

For nearly all of the reactions studied, it was not necessary to include the rate law for the autocatalytic reaction in order to obtain a good fit to the experimental data. There was a problem, however, in fitting the experimental concentration vs. time data for the reaction of methyl diethylphosphinite \((\text{Et}_2\text{POMe})\) with methyl iodide. It was necessary to use a large rate constant for the
Figure 2.5 Specific conductivity as a function of concentration for Et₃P⁺Me I⁻ in propylene carbonate at 25.0 °C. Linear equation.

The circles represent experimental data points. The solid line is the least squares fit of these points.
Table 2.3 Arbusov rearrangements studied, their phosphonium intermediates, and model salts used in calculations.

\[
\text{ABPOMe} + \text{MeI} \rightarrow \text{ABP}^+ (\text{OME})\text{Me} + \text{I}^- \rightarrow \text{ABP(O)Me} + \text{MeI}
\]

<table>
<thead>
<tr>
<th>ABPOMe</th>
<th>ABP+(OME)Me</th>
<th>model salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(MeO)$_3$P</td>
<td>(MeO)$_3$P$^+$Me I$^-$</td>
<td>Et$_3$P$^+$Me I$^-$</td>
</tr>
<tr>
<td>(MeO)$_2$PPh</td>
<td>(MeO)$_2$P$^+$PhMe I$^-$</td>
<td>Et$_2$P$^+$PhMe I$^-$</td>
</tr>
<tr>
<td>MeOPPh$_2$</td>
<td>MeOP$^+$Ph$_2$Me I$^-$</td>
<td>EtP$^+$Ph$_2$Me I$^-$</td>
</tr>
<tr>
<td>(MeO)$_2$PPh</td>
<td>(MeO)$_2$P$^+$PhMe I$^-$</td>
<td>Et$_2$P$^+$PhMe I$^-$</td>
</tr>
</tbody>
</table>
Figure 2.6 Ph₂P⁺(OMe)Me Concentration as a function of time for the reaction:

\[
\begin{align*}
\text{MeI} & \quad \xrightarrow{\text{Ph₂POMe}} \quad \text{Ph₂P(O)Me}
\end{align*}
\]

\[\text{[Ph₂POMe]}_0 = 0.2169 \text{ molar}\]

\[\text{[MeI]}_0 = 0.07110 \text{ molar}\]

The circles represent experimental data points. The solid curve is that obtained by numerical integration of the rate law.
autocatalytic reaction to obtain a good fit to the experimental data by numerical integration. This large rate constant was found to be in error when the autocatalytic reaction was monitored by $^{31}$P nmr as described later in this section. In order to determine the source of the discrepancy between the rate constants obtained from the two different methods, the reaction of methyl diethylphosphinite with methyl iodide was followed by $^{31}$P nmr. This method allows us to detect the changes in concentration occurring for all three phosphorus-containing species involved in the reaction. In this manner, we observed that all of the methyl diethylphosphinite was converted to phosphonium salt by the time the first spectrum was recorded. The only reaction observed was the conversion of the diethylmethoxymethylphosphonium iodide to the methyl diethyl phosphine oxide product. This result was rather surprising, since all of the other phosphorus esters studied underwent methylation by methyl iodide much more slowly than their salts decomposed to product. Formation of phosphonium salt is assumed to be the rate determining step for Arbuzov reactions involving methyl iodide. But in the case of methyl diethylphosphinite, the first step of the "textbook" mechanism is obviously much faster than the second. The rate of decay of diethylmethoxymethylphosphonium iodide was measured by observing the decrease in its $^{31}$P nmr signal. Because $k_1 \gg k_2$ for this reaction, equation (2.3) reduces to equation 2.10. The second order rate constant obtained
\[(2.10) \quad \frac{d[\text{ABP}^+(\text{OMe})\text{Me}]}{dt} = -k_2[\text{ABP}^+(\text{OMe})\text{Me}][\text{I}^-]\]

is \((7.60 \pm 0.15) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}\) for the reaction in propylene carbonate at 26.4 °C (temperature of the nmr probe). The nmr data clearly indicate that the methyl diethylphosphininite is converted nearly quantitatively into phosphonium salt which then slowly decomposes into the Arbuzov product. In the conductivity studies, however, the maximum salt concentration detected corresponded to only about 60% of the initial methyl diethylphosphininite concentration. We concluded that the need for a large autocatalytic rate constant in the analysis of the conductivity data was simply due to oxidation of this highly reactive phosphorus ester during preparation of the reaction solution. Therefore, the actual initial \(\text{Et}_2\text{POMe}\) concentration was less than that used in the numerical integration program to calculate the concentration vs. time data for the phosphonium salt.

In the light of this new information concerning the relative magnitudes of the rates for the two steps of the Arbuzov reaction, the conductivity data can be interpreted in a much simpler manner. The concentration vs. time data obtained after the maximum point should correspond to the second order decay of the phosphonium ion, according to equation 2.10. Those data fit a second order decay quite well \((r = 0.997)\); the value of \(k_2\) obtained for one run was \((3.51 \pm 0.08) \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}\). In addition, the actual initial concentration of methyl diethylphosphininite for each
conductivity experiment can be approximated by the concentration of phosphonium salt at its maximum. Using this approximation and the value obtained for $k_2$, the conductivity data were reinterpreted. The values for [$\text{Et}_2\text{POMe}]_0$, and $k_2$, were varied slightly from their "known" values, and $k_1$ values were varied to obtain the best fit to the experimental data. We feel that the rate constants obtained in this manner are nearly as accurate as those obtained from the other conductivity data since the nmr study provided us with good approximations to two of the variables involved. The rate constants, $k_1$ and $k_2$, obtained by conductivity are reported in table 2.4.

The reaction of trimethyl phosphite with methyl iodide was followed by $^{31}\text{P}$ nmr in order to confirm the rate constants obtained from the conductivity experiments. The phosphonium salt was not detected throughout the course of the experiment, and the disappearance of the trimethyl phosphite follows a first order reaction dependent upon the methyl iodide concentration. This indicates that $k_2 \gg k_1$ for this reaction, and the differential rate equation for the product, dimethyl methylphosphonate, reduces to equation (2.12).

\[(2.12) \frac{d[(\text{MeO})_2\text{P(OMe)}]}{dt} = k_1 [(\text{MeO})_3\text{P}]_0 - [(\text{MeO})_2\text{P(OMe)}]_t [\text{MeI}]\]

The second order rate constant for methylation of trimethyl phosphite by methyl iodide was obtained by dividing the
Table 2.4 Rate constants for the Arbuzov rearrangement obtained by conductivity

\[
\begin{align*}
\text{ABPOMe} + \text{MeI} & \xrightarrow{k_1} \text{ABP}^+(\text{OMe})\text{Me} + \text{I}^- \\
\text{ABP}^+(\text{OMe})\text{Me} + \text{I}^- & \xrightarrow{k_2} \text{ABP(O)Me} + \text{MeI}
\end{align*}
\]

in propylene carbonate at 25.0 °C

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>([\text{ABPOMe}]_0) (M)</th>
<th>([\text{MeI}]_0) (M)</th>
<th>(k_1 \times 10^3) (M(^{-1}) s(^{-1}))</th>
<th>(k_2) (M(^{-1}) s(^{-1}))</th>
<th>(k_2) per OMe group (M(^{-1}) s(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>MeO</td>
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<td>2.068</td>
<td>0.0725</td>
<td>49.7</td>
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<td>0.3732</td>
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<td>3.972</td>
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<td>MeO</td>
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<td>0.5104</td>
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<td>0.2255</td>
<td>0.0750</td>
<td>5.47</td>
<td>0.221</td>
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<td>&quot;</td>
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<td>0.02169</td>
<td>0.0711</td>
<td>5.47</td>
<td>0.208</td>
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<tr>
<td>Et</td>
<td>Et</td>
<td>0.0039</td>
<td>0.04442</td>
<td>170</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>0.0085</td>
<td>0.02165</td>
<td>180</td>
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pseudo first order rate constant by the methyl iodide concentration which remains essentially constant throughout the experiment. The rate constant obtained for the reaction in propylene carbonate at 26.4 °C is (1.22 ± .03) x 10⁻⁴ M⁻¹s⁻¹ (r = 0.997) which agrees well with the value obtained by conductivity. The experimental data for this reaction are reported in Appendix I.

In order to obtain rate constants for the autocatalytic reaction (equation 2.3), these reactions were studied independently by ³¹P nmr. The phosphorus ester was added to a solution of the methoxyphosphonium triflate in propylene carbonate. Under these conditions, the only reaction which can occur is autocatalysis, since the triflate anion is too poor a nucleophile to convert the phosphonium salt to the Arbuzov product.⁵¹ The peak for the phosphorus ester decreases as the peak for the Arbuzov product increases with time. Figure 2.7 shows the spectra resulting from a typical experiment; the fit of the data to a kinetic plot (as described below) is shown in figure 2.8. Additional data for these studies are reported in Appendix I. The differential rate equation for the autocatalytic reaction is given in equation (2.13).

\[
\frac{d[\text{ABPOMe}]}{dt} = -k_3[\text{ABPOMe}][\text{ABP}^\cdot(\text{OME})\text{Me}]
\]

The second order rate constants, \( k_3 \), are obtained by dividing the pseudo first order rate constants by the
Figure 2.7  $^{31}$P nmr spectra for the reaction:

$$\text{PhP}^+(\text{OMe})_2\text{Me} \xrightarrow{} \text{PhP}(\text{O})(\text{OMe})\text{Me}$$

in propylene carbonate at 26.4 °C

$[\text{PhP}(\text{OMe})_2]_0 = 0.2347$ molar

$[\text{PhP}^+(\text{OMe})_2\text{Me}] = 0.1206$ molar
Figure 2.8 Kinetic plot for the reaction

\[
\text{PhP}^+\text{OMe}_2 \rightarrow \text{PhP(OMe)Me}
\]

in propylene carbonate at 26.4 °C

\[\text{[PhP(OMe)_2]}_o = 0.2347 \text{ molar}\]

\[\text{[PhP}^+\text{(OMe)}_2\text{Me]}_o = 0.1206 \text{ molar}\]

The circles represent experimental data points. The solid line is the least squares fit of these points.
phosphonium ion concentration which remains essentially constant throughout the experiment. Table 2.5 reports the rate constants obtained in this manner for the same series of phosphorus esters that were studied by conductivity. The combined rate constants obtained from conductivity and $^{31}$P nmr are shown in table 2.6.
Table 2.5 Rate constants of the autocatalytic Arbuzov reaction obtained by $^{31}$P nmr.

\[
ABPOMe + ABP^+(OMe)Me \rightarrow ABP^+(OMe)Me ABP(O)Me
\]

in propylene carbonate at 26.4 °C.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>[ABPOMe]₀ (M)</th>
<th>[ABP⁺(OMe)Me] (M)</th>
<th>$k_{obs} \times 10^4$ (s⁻¹)</th>
<th>$k_3 \times 10^3$ (M⁻¹ s⁻¹)</th>
<th>$k_3 \times 10^3$ per OMe group (M⁻¹ s⁻¹)</th>
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<td>MeO</td>
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<td>0.09751</td>
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<td>&quot;</td>
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<td>5.64</td>
<td>1.88</td>
</tr>
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<td>&quot;</td>
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<td>MeO</td>
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<tr>
<td>Et</td>
<td>Et</td>
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<td>&quot;</td>
<td>0.3789</td>
<td>0.07163</td>
<td>5.38</td>
<td>0.751</td>
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</tbody>
</table>
Table 2.6 Rate constants for the MeI catalyzed and autocatalyzed Arbuzov rearrangement

\[
\begin{align*}
\text{ABPOMe} + \text{MeI} & \xrightarrow{k_1} \text{ABP}^+(\text{OMe})\text{Me} + \text{I}^- \\
\text{ABP}^+(\text{OMe})\text{Me} + \text{I}^- & \xrightarrow{k_2} \text{ABP}(\text{O})\text{Me} + \text{MeI} \\
\text{ABPOMe} + \text{ABP}^+(\text{OMe})\text{Me} & \xrightarrow{k_3} \text{ABP}(\text{O})\text{Me} + \text{ABP}^+(\text{OMe})\text{Me}
\end{align*}
\]

in propylene carbonate

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>$k_1 \times 10^3$ (M$^{-1}$ s$^{-1}$)$^a,b$</th>
<th>$k_2$ per OMe group (M$^{-1}$ s$^{-1}$)$^a,b$</th>
<th>$k_3 \times 10^3$ per OMe group (M$^{-1}$ s$^{-1}$)$^a,c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>0.0825 ± 0.0232</td>
<td>17.5 ± 2.25</td>
<td>1.88 ± 0.01</td>
</tr>
<tr>
<td>OMe</td>
<td>Ph</td>
<td>1.86 ± 0.10</td>
<td>2.09 ± 0.13</td>
<td>2.54 ± 0.13</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>5.59 ± 1.32</td>
<td>0.397 ± 0.088</td>
<td>1.46 ± 0.04</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>5.69 ± 0.38</td>
<td>0.217 ± 0.008</td>
<td>1.37 ± 0.28</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>175 ± 7</td>
<td>0.00480 ± 0.00042</td>
<td>0.735 ± 0.023</td>
</tr>
</tbody>
</table>

$^a$ Values reported are the mean ± S.D. for at least two independent runs of the same compound.
$^b$ T = 25.0 °C.
$^c$ T = 26.4 °C.
Discussion

To our knowledge, this study comprises the first correct application of electrical conductivity in the study of the Arbuzov rearrangement. Two groups of workers had previously attempted use this technique to measure rates of the Arbuzov reactions of trialkylphosphites\textsuperscript{79,80}, however; their interpretation of the experimental data was seriously in error. They assumed that the conductivity vs. time data (which follows a fast rise and slow decay) indicated that $k_1 \gg k_2$; and interpreted their data on the basis that the trialkoxyphosphonium ion was formed quantitatively and slowly decomposed to product. However, from our study of the reaction of trimethyl phosphite with methyl iodide, the maximum concentration of methyltrimethoxyphosphonium iodide detected during the experiment is only 0.2\% of the initial trimethyl phosphite concentration! Larger concentrations of trialkoxyphosphonium ions were probably reached in their experiments due to the slower rate of reaction of iodide anion with higher alkoxy groups\textsuperscript{30}, but quantitative yields are impossible since $k_2 \gg k_1$ for these compounds.\textsuperscript{32}

From inspection of the differential rate equation describing the concentration of the phosphonium intermediate, it is apparent that the position of the maximum conductivity is dependent on the ratio $k_1/k_2$ (in addition to the initial concentration of the reactants). Thus, the "rise" of the conductivity vs. time curve will be
"fast" for reactions with a small ratio (small $k_1$, large $k_2$) and "slow" for compounds with a large ratio (large $k_1$, small $k_2$). In fact, in two cases, trimethyl phosphite ($k_1/k_2 = 1.6 \times 10^{-6}$) and dimethyl phenylphosphonite ($k_1/k_2 = 4.5 \times 10^{-4}$), the maximum conductivity was reached too fast to be seen in the time scale involved in transferring the reaction solution to the conductivity cell (approximately 3 to 4 minutes). It is interesting to note that if these workers had studied alkyl dialkylphosphinites, it is likely that their interpretation of the results would have been correct.

In this study we treat quantitatively a species undetectable by most other analytical methods that have previously been used to study the Arbuzov reaction. The maximum methoxyphosphonium iodide concentration detected in these reactions ranges from 0.2% to nearly 100% that of the starting phosphorus ester concentration. Since our derived rate constants are based only on concentration data for the intermediate of the reaction, care was taken to insure that the reactions were occurring as we had expected. The experimental controls used are described in further detail in the experimental section. As pointed out in the introduction, there is a substantial body of evidence supporting the intermediacy of phosphonium ions in Arbuzov reactions. We are also confident that the mechanism of the reactions studied consists of sequential bimolecular substitution reactions.
By monitoring the concentration of the intermediate, we were able to study both steps of the Arbuzov rearrangement occurring simultaneously. This is only the second such study$^{51}$, and the first for a reaction involving a nucleophile as strong as iodide. The bulk of the previous studies consist of measurements of only one step of the "textbook" mechanism due to the limitations of the available experimental methods.

Values of $k_1$ have been obtained by such techniques as $^1$H and $^{31}$P nmr spectroscopy$^{51}$, gas chromatography$^{33}$, and infrared spectroscopy$^{32}$. The rate constants obtained from our conductivity studies show no large deviation from those determined by other workers when differences in temperature and solvent are considered. The closest available data for comparison is the work of Lewis and Hamp for the reactions of PhP(OMe)$_2$ and EtP(OMe)$_2$ with methyl iodide in CH$_3$CN at 34.4 oC.$^{51}$ Their rates of $1.2 \times 10^{-3}$ M$^{-1}$s$^{-1}$ and $4.0 \times 10^{-3}$ M$^{-1}$s$^{-1}$ respectively are slightly lower than our values of $1.86 \times 10^{-3}$ M$^{-1}$s$^{-1}$ and $4.81 \times 10^{-3}$ M$^{-1}$s$^{-1}$. The higher reaction rates that we obtained at a lower temperature are probably the result of a solvent effect (the higher dielectric constant of propylene carbonate enables this solvent to stabilize the developing positive charge of the transition state better than CH$_3$CN). Our $k_1$ values are in general larger than rates obtained by other workers in benzene$^{33}$, CH$_3$CN$^{32}$, and CDCl$_3$.$^{51}$. 
Our rate constants for the decomposition of methoxyphosphonium iodides are clearly second order. The experimental data cannot be fit by a first order rate constant for $k_2$. The requirements of high solvent polarity and low concentration that appear to be necessary for dissociation of the intermediate phosphonium ions are met by our experimental conditions.

There are little available kinetic data on the decomposition of alkoxyphosphonium ions under second order conditions. Nesterov and Aleksandrova found a second order rate constant of $4.25 \times 10^{-6}$ M$^{-1}$s$^{-1}$ for decomposition of $EtP^+(isoBu)Me I^-$ in CH$_3$CN.$^{39}$ Extrapolating this value to 25.0 °C gives $k_2 = 6.67 \times 10^{-6}$ M$^{-1}$s$^{-1}$ which after correction for the lower reactivity of isobutyl compared to methyl in $S_n2$ reactions (the relative reactivity of isobutyl to methyl is $1 \times 10^{-4}$ $^{30}$) becomes 0.0667 M$^{-1}$s$^{-1}$. This figure is significantly lower than our $k_2$ value of 0.397 M$^{-1}$s$^{-1}$ (uncorrected for two methoxy groups) for $EtP^+(O\text{Me})_2\text{Me} I^-$. A slightly higher rate constant is expected for decomposition of the phosphonium salt in CH$_3$CN since charge is dispersed in going from reactants to transition state, and a less polar solvent is expected to accelerate the reaction more than a very polar solvent. The lower reactivity of the diisobutyl compound is probably due to a steric effect; the bulk of the nonreacting isobutyl substituent may hinder attack by the iodide ion. The rate constants for the reaction of unhindered methoxyphosphonium ions with iodide
haven't been determined as yet, except for an estimation of 900 M\(^{-1}\)s\(^{-1}\) for the reaction of methyltrimethoxyphosphonium ion with iodide at 0 °C in acetone.\(^{22}\) The large discrepancy with our value of 57.5 M\(^{-1}\)s\(^{-1}\) is probably due here to the method used to follow the reaction in acetone -- the Bell temperature rise method. It is estimated that reactions with rate constants greater than 5 - 6 M\(^{-1}\)s\(^{-1}\) are too fast for accurate determination of the rate constant by this method and that the accuracy decreases with increasing rate of reaction.\(^{81}\) The rate of reaction of methyltrimethoxyphosphonium ion with iodide is much greater than this, which may result in an inaccurate rate measurement by the Bell method.

There has been only one quantitative study of the autocatalytic Arbuzov rearrangement.\(^{51}\) A comparison of our values of \(k_3\) to those of Lewis and Hamp\(^{51}\) reveals that they are slightly lower than the same reactions measured in CD\(_3\)CN at 34.4 °C, but usually much lower than the reactions measured in CDC\(_1\)l\(_3\) at 26.8 °C. This difference is probably due to a solvent effect. Since there is a dispersal of charge in going from reactants to the transition state, the reaction should be accelerated by less polar solvents in which the reacting phosphonium salt is destabilized as in the second step of the "textbook" mechanism. Our data constitute a significant advance in the study of this very interesting aspect of the Arbuzov reaction. Although the precision possible from \(^{31}\)P nmr analysis does not approach
that of other methods (for a detailed discussion on the use on $^{31}\text{P}$ nmr as a quantitative tool, see reference 46), it is a convenient way to follow this reaction and is a method being used with increasing frequency in organophosphorus chemistry.\textsuperscript{12,14,39}

Since the first step of the "textbook" mechanism, methylation of the trivalent phosphorus ester, is an $S_{N}2$ reaction, its transition state will consist of partial bond formation between the phosphorus atom and the methyl group and partial bond breaking between the methyl group and the iodine atom as shown in figure 3.1.\textsuperscript{82} The rate of the reaction will be dependent on the stabilization of the transition state (figure 3.1) by the substituents attached

\begin{equation}
\begin{array}{c}
\text{A} \\
\text{B-P} \cdots \cdots \text{CH}_3 \cdots \cdots \text{I} \cdots \\
\text{MeO}^-
\end{array}
\end{equation}

\text{figure 3.1}

to phosphorus. The rates can thus be correlated using a modified Taft linear free energy relationship (equation 3.1).\textsuperscript{83} $\sigma_\text{I}$ is a measure of the inductive effect of the

\begin{equation}
\log(k/k_0) = \rho_\text{I}\sigma_\text{I} + \rho_\text{R}\sigma_\text{R} + \delta\Sigma_\text{E}
\end{equation}

substituents attached to phosphorus\textsuperscript{84}, $\sigma_\text{R}$ is the combined ability of the substituents to delocalize either excess electron density or a positive charge away from
phosphorus, and is the combined steric requirements of the substituents. The values of $\rho_I$, $\rho_R$, and $\delta$ are measures of the sensitivity of the transition state to inductive, resonance, and steric effects respectively. The $\sigma_I$ values were originally defined for reactions at carbon centers and are generally used as a method of quantitation of the inductive effects occurring through C-C σ bonds. They have, however, been successfully applied in linear free energy studies involving reactions at nitrogen, sulfur, and phosphorus.

It is fairly well established that resonance and steric effects play an insignificant role in the chemistry of reactions involving phosphorus. Resonance interaction between the $\pi$ electron system of phenyl groups and the d orbitals of phosphorus appears to be excluded by the P-Ph bond length which is marginally longer on the average than the P-CH$_3$ bond length. If resonance were important, we would expect the P-Ph bond length to be significantly shorter. It also seems unlikely that there is significant $p\pi$-$d\pi$ interaction between the oxygen lone pairs and the phosphorus atom of alkoxy substituted phosphorus compounds. The stability of alkoxyphosphonium ions increases in the series MeP$^+$ (OR)$_3$ $<$ MePhP$^+$ (OR)$_2$ $<$ Me(Ph)$_2$P$^+$ OR $/$, while the reverse would be expected if $p\pi$-$d\pi$ interaction were occurring. The stability order in the series is attributed mainly to the inductive effect of the substituents; the electron withdrawing alkoxy groups destabilize the
positively charged ion while the electron donating phenyl groups stabilize it. Further evidence is the Hammett correlation for reactions of triarylphosphines containing electron accepting substituents in the para position of the phenyl ring. The rates of reaction on phosphorus correlate with $\sigma_I$ not $\sigma^+$ or $\sigma^-$ which establishes that there is no appreciable mesomeric interaction between phosphorus and its substituents in these reactions.\textsuperscript{92} There is also no evidence of hyperconjugation ($\sigma-d$ conjugation as in figure 3.2) in phosphorus compounds containing alkyl substituents,

\begin{equation}
\begin{array}{c}
\text{A} \\
\text{B-P}^+CH_2 \\
\text{C}^-
\end{array} \leftrightarrow \begin{array}{c}
\text{A} \\
\text{B-P}^-CH_2 \\
\text{C}^-
\end{array}
\end{equation}

**figure 3.2**

since a consequence of this would be an increase in the basicity of phosphines containing methyl groups.\textsuperscript{93} However, the basicity of phosphines decreases in the series \((\text{Me})_2\text{PET} > \text{Et}_2\text{PMe} > \text{Me}_3\text{P}\)\textsuperscript{94}, while an order of \(\text{Me}_3\text{P} > \text{Me}_2\text{PET} > \text{MePBT}_2\) would be expected if hyperconjugation effects were dominant. It is likely, however, that the marked stability of phosphonium ions containing dialkylamino groups compared to alkoxyphosphonium ions is due to $\pi-d\pi$ interaction.\textsuperscript{95}

The large size of the phosphorus atom ensures low steric hindrance due to atoms and groups attached to it (the covalent radius of trivalent phosphorus is 1.1 Å as compared to 0.77 for carbon and 0.70 for nitrogen\textsuperscript{96}). Steric effects
are thought to operate only in alkylation reactions of phosphorus compounds containing alkyl groups higher than propyl; tervalent phosphorus compounds such as those we studied containing small alkyl groups or phenyl rings are thought to be unhindered. Thus, only $\Sigma \sigma_I$ is necessary for the correlation. The $\sigma_I$ values used in the correlations ($Et = -0.05$, $OMe = 0.27$, $Ph = 0.10$) are those of J. Hine. The Taft plot of the $k_1$ values is shown in figure 3.3 (a value for the reaction of triphenylphosphine with methyl iodide obtained in an unrelated study is included). The $\rho_I$ obtained is $-4.6 \pm 0.6$ indicating, as expected, that electron supplying substituents attached to the phosphorus atom increase the rate ($k_1$) of the reaction by inductively stabilizing the developing positive charge on phosphorus in the transition state. Although the range of $\Sigma \sigma_I$ values covered is small ($0.17 - 0.81$), the reactivity range is large (greater than a factor of $10^6$). The correlation is quite satisfactory ($r = 0.968$) which further confirms the lack of resonance or steric effects in this series. The deviations appear to be random, that is, in no predictable direction for a given substituent.

The value of $\rho_I$ can be used to estimate the extent of bond making and bond breaking in the transition state according to equation 3.2. $p$ refers to the position of $p = E_a / (2E_a - \Delta H) = \rho^+/\rho_{eq}$
Figure 3.3  Taft plot for the reaction:

$$ABPOMe + MeI \xrightarrow{k} ABP^{+}(OMe)Me + I^-$$

in propylene carbonate at 25.0 °C
the transition state along the reaction coordinate, $E_a$ is the activation energy of the forward reaction, $\Delta H$ is the enthalpy of the forward reaction, $\rho^+$ is the sensitivity of the forward reaction to substituents, and $\rho_{eq}$ is the sensitivity of the equilibrium constant to substituents.

For very exothermic reactions, $-\Delta H > E_a$ and $p = 0$ indicating a reactant-like transition state. For very endothermic reactions, $E_a = \Delta H$ and $p = 1$ indicating a product-like transition state. Thus, equation 3.2 is in agreement with the Hammond postulate. A value of $p = 0.5$ corresponds to a structured transition state with equal bond formation and bond breaking.

Hamp$^{46}$ has calculated $\rho_{eq}$ for the protonation of tertiary phosphines from the data of Henderson and Streuli$^{94}$ in H$_2$O and Stepanov$^{100}$ in CH$_3$NO$_2$ to be 21 and 17 respectively. Assuming that $\rho_{eq}$ (CH$_3$) = $\rho_{eq}$ (H), gives a value of $p = 0.22$ (H$_2$O) or 0.27 (CH$_3$NO$_2$). The "true" value is probably somewhere in between since the dielectric constant of propylene carbonate is between that of CH$_3$NO$_2$ and H$_2$O. This value of $p$ corresponds to the development of about one-quarter of a positive charge on phosphorus in the transition state, or about one-quarter bond making between the phosphorus and the methyl group.

Our $\rho_I$ for the first step of the "textbook" mechanism compares well to that calculated by Hamp from his data and those of other workers.$^{46}$ He obtained a $\rho_I = -3.8$ for reactions of trivalent phosphorus compounds with methyl
iodide. Most of the data was obtained in CH₃CN at 25 - 30 °C. Our slightly larger value corresponds to greater charge development in the transition state which is probably due to better solvation of the positive charge by propylene carbonate than CH₃CN.

The second step of the "textbook mechanism" can also be correlated using equation (3.1). Here, the rate will be dependent upon the degree of stabilization of the phosphonium salt by the substituents attached to phosphorus (figure 3.4). The charge on phosphorus decreases in going

\[
\begin{array}{c}
A \quad \delta^+ \\
B - \text{P} :: \text{O} \cdots \cdots \text{CH}_3 \cdots \cdots \text{I} \delta^- \\
\text{Me}
\end{array}
\]

\[\dagger\]

figure 3.4

from reactant to transition state, so that the stabilization due to the substituents will not be as important in the transition state as in the reactant. Therefore, we expect to see that phosphonium salts with electron donating substituents react slower (more stabilization of phosphonium salt) than phosphonium salts with electron withdrawing substituents. This is confirmed by our data which give a value of \( \rho_I \) of 5.60±0.18. The correlation here is very good with a correlation coefficient of 0.999. The Taft plot is shown in figure 3.5. The value of \( \rho_I \) also agrees with the known greater stability of phosphonium ions with electron donating substituents (alkyl, aryl, dialkylamino) over those
Figure 3.5 Taft plot for the reaction:

\[ \text{ABP}^+\text{(OMe)Me} + \text{I}^- \xrightarrow{k_2} \text{ABP(O)Me} + \text{MeI} \]

in propylene carbonate at 25.0 °C
with electron attracting substituents (alkoxy, aryloxy).\textsuperscript{101} For this reaction, \( p \) can be calculated as was done for the methylation of phosphorus esters. Lewis and Colle measured the equilibrium constants \( (K_{eq}) \) for the methylation of trifluoromethanesulfonate anion by methoxyphosphonium ions in \( \text{CCl}_4.\textsuperscript{50} \) A plot of \( \log K_{eq} \) vs. \( \Delta G^\ddagger \) results in a slope of \( 9.84 = \rho_{eq} \ (r = 0.93) \). Assuming that \( \rho_{eq} (\text{OSO}_2\text{CF}_3) = \rho_{eq} (I^-) \), gives a \( p \) value for this reaction of 0.58, which corresponds to nearly equal bond formation and bond breaking in the transition state or, likewise, to transfer of one-half of a positive charge. Similarly, a small \( \alpha \text{-deuterium isotope effect} \ (1.05) \) has been observed in decomposition of \( (\text{CH}_3)_3\text{CCH}_2\text{OP}^+(\text{Ph})_3\text{Cl}^- \) in \( \text{CHCl}_3 \); which has been interpreted as an indication that the transition state consists of nearly equal bond making and bond breaking.\textsuperscript{41}

In the autocatalytic reaction, the above mentioned effects occur simultaneously (figure 3.6). The phosphorus ester will be affected by substituents, and its rate of

\[
\begin{bmatrix}
\text{A} \overset{+}{\text{P}} & \overset{-}{\text{Me}} \\
\text{B} & \overset{-}{\text{OMe}}
\end{bmatrix}
\]

\text{figure 3.6}

attack on the phosphonium salt will be dependent on the stabilization of its developing positive charge in the transition state. The rate of reaction of the salt is also dependent on the substituents attached to phosphorus but in
an opposing manner to that of the phosphorus ester. For example, electron supplying substituents will cause the phosphorus ester to react faster, but will also stabilize the salt to attack. From the values of $\rho_1$ and $\rho_2$ (where the superscript denotes the rate constant from which the $\rho_I$ value is obtained), however, we can expect that the overriding effect will be the stabilization of the phosphonium salt. This is confirmed by a value of $\rho_3 = 0.754 \pm 0.228$ for our data. The Taft plot for the autocatalytic reaction is shown in figure 3.7. Although the correlation of $\Sigma \rho_I$ to our rate constants $k_3$ is rather poor ($r = 0.886$), we believe that this is due to the problems associated with quantitating $^{31}$P nmr and the lack of precision in rate constants obtained from this method. Also, the range of reactivities is very small (less than a factor of ten), and the substituent effect is correspondingly low as expected for the opposing effects involved.

Because the autocatalytic reaction is merely the sum of the two steps of the "textbook" mechanism, we can obtain $\rho_3$ from the sum of $\rho_1$ and $\rho_2$ ($-4.6 + 5.6 = 1.0$). The value obtained in this manner is nearly equal to that derived experimentally. This provides a suitable check on our value of $\rho_3$ since there is no data available in the literature with which to compare it. Lewis and Hamp were unable to determine the substituent effect on the autocatalytic reactions that they studied, although the rate constants
Figure 3.7 Taft plot for the reaction:

\[
\text{ABPOMe} + \text{ABP}^+(\text{OMe})\text{Me} \xrightarrow{k_3} \text{ABP(O)Me} + \text{ABP}^+(\text{OMe})\text{Me}
\]

in propylene carbonate at 26.4 °C
showed little variation with substituents\textsuperscript{51} which is confirmed by the small $\rho_I$ obtained in this study.

Kabachnik\textsuperscript{93} has defined a set of substituent parameters, $\sigma^{ph}$, for substituents attached to phosphorus. These are, however, considered to be applicable only in reactions not directly involving the phosphorus atom. We found that our data correlate slightly better to the Taft substituent parameters, $\sigma_I$, than Kabachnik's $\sigma^{ph}$, although the difference is very small.

This method can be extended to a wide variety of Arbuzov reactions utilizing different alkylating agents and trivalent phosphorus esters. The alkylphosphonium salts to be used as analogs for determining the concentration dependence of the conductivity of the intermediate alkoxlyphosphonium salts can in principle be easily synthesized for any reaction. Care must be taken when choosing the solvent and concentrations to insure that the intermediate phosphonium ions are completely dissociated. Inspection of figures 2.2 - 2.4 also reveals that the linear relationship of conductivity to concentration will not be accurate for concentrations of phosphonium ions much greater than 0.01 molar.

The information obtained in this study indicates that all reactions are bimolecular $S_{N}2$ reactions. The most important overall factor determining the reactivity is the inductive effect of substituents on the stability of phosphonium salts. The rate determining step can even be
changed from the first step (as was observed in all other Arbuzov reactions with methyl iodide) to the second when two alkyl groups are present on the phosphorus ester.

This new information on the reactivity of organo-phosphorus compounds in the Arbuzov rearrangement is certainly of significance. A better understanding of the factors affecting the reactivity of phosphorous esters in their conversion to phosphonates can increase the synthetic utility of the Arbuzov reaction. In many cases it is desirable to run this reaction under the mildest possible conditions to avoid the destruction of other organic functional groups present. Any information which will determine the optimal conditions for reactions can lead to better synthetic results.
Experimental

Materials:

Propylene carbonate (99% from Aldrich Chemical Company) was twice vacuum distilled at 8-10 torr and stored under nitrogen until used. This procedure was sufficient to give propylene carbonate with undetectable conductivity on the system described below. Methyl diethylphosphinite, methyl diphenylphosphinite, dimethyl ethylphosphonite, and dimethyl phenylphosphonite were obtained commercially (Strem Chemical Company) and used without further purification. The identity and purity of each was checked by $^{31}P$ NMR before use. Trimethyl phosphite (97% from Aldrich Chemical Company) was treated with sodium followed by distillation under nitrogen: bp 112°C. The trivalent phosphorus esters are moisture and air-sensitive and should be stored and transferred under nitrogen to avoid contamination. Methyl iodide was distilled under nitrogen from P2O5: bp 41°C. Methyl trifluoromethanesulfonate (methyl triflate) was obtained commercially (99+% from Aldrich Chemical Company) and used without further purification. Methyl iodide and methyl triflate are both powerful methylating agents and should be handled with care.

Synthesis of Phosphonium salts:

The methoxyphosphonium trifluoromethanesulfonate (triflate) salts were prepared following the procedure of
Lewis and Colle.\textsuperscript{21} Five of the triflate salts (dimethoxyethylmethyl, dimethoxymethylphenyl, diphenylethylmethyl, diethylmethoxyethylmethyl, and diphenylmethoxyethylmethyl) prepared were oils which, after removal of the solvent under vacuum, solidified upon storage at 0 °C. The other two triflate salts (diethylmethylphenyl and methyltrimethoxy) were obtained as white precipitates and were filtered and washed with anhydrous ether in a dry box. The phosphonium iodides (methyltriethyl, diethylmethylphenyl, diphenylethylmethyl) were prepared by methylation of the commercial phosphines with methyl iodide in the same manner as the triflates. These salts were obtained as fine white precipitates which were recrystallized from EtOH/Ether (diphenylethylmethylphosphonium iodide, diethylmethylphenylphosphonium iodide) or isopropanol (methyltriethylphosphonium iodide). The purity of the phosphonium salts was determined by their melting points (taken under nitrogen) and $^1$H and $^{31}$P NMR spectra (obtained on a JEOL FX-90Q instrument operating in the fourier transform mode). Three of the phosphonium triflates were unknown compounds, but their hydroscopic nature and difficulty in purification made elemental analysis impractical. The high resolution mass spectrometry reports (for exact mass determination of the phosphonium cation) and $^1$H nmr spectra for these compounds are reported in Appendix II. The uncorrected melting points and $^{31}$P chemical shifts for all phosphonium salts are reported in Table 4.1.
Table 4.1 Melting points and $^{31}$P chemical shifts of phosphonium salts $\text{ABCP}^+\text{Me} X^-$

| $\text{ABCP}^+\text{Me}$ | $X^-$ | mp (°C) | $\delta^{31}\text{P}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{MeO})_2\text{P}^+\text{Me}$</td>
<td>OTf$^-$</td>
<td>49-50 (lit.$^b$ 28-32)</td>
<td>53 (lit.$^b$ 53.1)</td>
</tr>
<tr>
<td>$(\text{MeO})_2\text{P}^+\text{PhMe}$</td>
<td>OTf$^-$</td>
<td>28.5-30 (lit.$^b$ oil)</td>
<td>78 (lit.$^b$ 78.5)</td>
</tr>
<tr>
<td>$(\text{MeO})\text{P}^+\text{Ph}_2\text{Me}$</td>
<td>OTf$^-$</td>
<td>52-54 (lit.$^b$ 34-37)</td>
<td>75 (lit.$^b$ 74.5)</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}^+\text{Me}$</td>
<td>OTf$^-$</td>
<td>87-90</td>
<td>37.3</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}^+\text{PhMe}$</td>
<td>OTf$^-$</td>
<td>41-46</td>
<td>32.4</td>
</tr>
<tr>
<td>$\text{EtP}^+\text{Ph}_2\text{Me}$</td>
<td>OTf$^-$</td>
<td>~22</td>
<td>26.2</td>
</tr>
<tr>
<td>$(\text{MeO})_2\text{P}^+\text{EtMe}$</td>
<td>OTf$^-$</td>
<td>35-37 (lit.$^b$ ~0)</td>
<td>99 (lit.$^b$ 99)</td>
</tr>
<tr>
<td>$\text{MeOP}^+\text{Et}_2\text{Me}$</td>
<td>OTf$^-$</td>
<td>36-39 (lit.$^b$ ~0)</td>
<td>104 (lit.$^b$ 103.5)</td>
</tr>
<tr>
<td>$\text{Et}_3\text{P}^+\text{Me}$</td>
<td>I$^-$</td>
<td>307-311 (lit.$^c$ 300-302)</td>
<td>37 (lit.$^d$ 37)</td>
</tr>
<tr>
<td>$\text{Et}_2\text{P}^+\text{PhMe}$</td>
<td>I$^-$</td>
<td>110-112 (lit.$^e$ 110)</td>
<td>32.7</td>
</tr>
<tr>
<td>$\text{EtP}^+\text{Ph}_2\text{Me}$</td>
<td>I$^-$</td>
<td>188-190 (lit.$^f$ 183)</td>
<td>26.4</td>
</tr>
</tbody>
</table>

---

a. Chemical shifts reported are downfield from an 85% $\text{H}_3\text{PO}_4$ reference for solutions of the phosphonium salts in CDCl$_3$.
b. Reference 22.
c. Reference 102.
d. Reference 7.
e. Reference 103.
f. Reference 104.
Conductivity Measurements:

Conductivities were measured using a Fischer brand enclosed conductivity cell with platinized electrodes (cell constant $0.250 \pm 0.003 \text{ cm}^{-1}$), a General Radio conductivity bridge (Model 1603-A), an oscillator operated at 1000 Hz with an applied voltage of 0.50 volts across the bridge with the bridge imbalance detected with an oscilloscope. The cell was immersed in a 25.0 °C thermostat; all conductivity measurements were taken at this temperature. The cell electrodes were platinized according to the procedure of Davies.\textsuperscript{105} The cell constant was determined in the usual manner\textsuperscript{106} using a standard potassium chloride solution (0.0100M from Anderson Laboratories Inc.). Propylene carbonate was chosen as a solvent only because it is the solvent we found with minimal reaction with methyl iodide, a reaction which turned out to be a consequence of using too high a voltage and too low a frequency on a different conductivity bridge, and not a property of the solvent. Thus, there is no reason to believe that several other aprotic solvents rejected earlier (sulfolane, methyl acetate, CH$_3$NO$_2$, and CH$_3$CN) would not have worked well with the proper bridge. The electrodes also were platinized during this preliminary bridge problem; there is no reason to believe that it is necessary. To obtain the concentration dependence of the conductivity for the phosphonium iodides and triflates, an approximately 0.01 molar solution of each salt in propylene carbonate was
prepared; this was diluted to obtain solutions of approximately 0.001, 0.003, 0.005, 0.007, and 0.009 molar concentration. The conductivities were measured (keeping the cell away from light for measurements of the phosphonium iodides) after the solution had been allowed to reach the temperature of the thermostat.

Conductivity Kinetic Experiments:

The reaction mixtures were prepared at room temperature by mixing the two reagents (either as stock solutions in propylene carbonate or by addition of the neat compounds) in propylene carbonate in a 25 ml volumetric flask. After mixing, approximately 15 ml of the solution were transferred to the conductivity cell (previously purged with nitrogen and placed in the thermostat). All transfers were performed under nitrogen, and the cell was kept under nitrogen and away from light during the course of the experiments. Measurements of the conductivity were made at frequent intervals. The possibility of a reaction occurring at the cell electrodes was ruled out by the addition of a few milliliters of the starting reaction solution (kept under nitrogen and away from light) to the conductivity cell after the reaction was nearly complete. In all cases, the conductivity changed by a negligible amount. Each reaction solution was allowed to remain in the cell until the conductivity no longer changed (in each case the final conductivity was less than 10% of the maximum conductivity
for that run, except in the case of trimethyl phosphite which had a very low conductivity), and at that point a $^{31}$P NMR was taken. In each case, only one phosphorus-containing compound was detected which had an appropriate chemical shift for the product. The ability to generate large amounts of data points (up to 78 per kinetic run depending upon the rate of the reaction) made the use of computer calculations extremely useful. The conductivity and time data points are entered into the program "ARBUZOV" (Appendix III) which calculates the concentration of the phosphonium ion intermediate for each data point. This data are then interpolated using the program "INTERP" (Appendix III) to obtain concentration vs. time data at even time intervals needed for use of the numerical integration program, KUT6NON\(^46\). The experimental concentration vs. time data and appropriate rate constants for each reaction are first entered into the program to obtain calculated concentration vs. time data for the intermediate phosphonium ion. Those data are compared to the experimental data, and the rate constants (also \([\text{Et}_2\text{P(OMe)}]\) in case of methyl diethyl-phosphinite) are changed until the best fit to the experimental data is obtained (as judged by the magnitude of the root mean square error between the calculated and experimental data). Because the "KUT6NON" program encountered floating point errors in running the data for the reaction of trimethyl phosphite, a different numerical integration program (kindly provided by Professor David
Stanbury of Rice University) was used to obtain the reported rate constants. The procedure used to obtain the rate constants is identical to that described above; this program was also used for another reaction to verify that the results are the same. The rate constants reported in Tables 2.4 and 2.6 are those which gave the best fit to the experimental data.

$31P$ NMR Kinetics:

All $31P$ FT NMR spectra were obtained on a Jeolco FX-90Q instrument, operated at 36.2 MHz. Acquisition parameters used for the kinetic studies include a 90° pulse width of 10.00 microseconds and a pulse delay of 5 seconds. All $31P$ nmr spectra were broadband proton decoupled. The reaction solutions were prepared at room temperature under nitrogen by addition of the neat compounds to propylene carbonate in a 10 ml volumetric flask. The solution was transferred under nitrogen to a 10 mm nmr tube with a concentric capillary tube containing (MeO)$_3$P(O) (as an external reference and standard for concentration determination when necessary) in acetone d-6 or benzene d-6 (as an external deuterium lock). This was necessary because 85% D$_3$PO$_4$/D$_2$O did not provide a suitable lock for the nmr.

It has been determined in this laboratory that peak height is proportional to concentration in many $31P$ nmr spectra. The validity of equation (4.1) was proved.$^{46}$

(4.1) $RPH \times M = (\text{concentration of phosphorus compound})$
Where \( RPH \) is the relative peak height of the phosphorus compound and \( M \) is the concentration/unit factor which will vary for different phosphorus compounds but remain the same for each compound within an nmr experiment. The relative peak height is the peak height relative to an external standard whose concentration does not change. It is necessary to use relative peak heights in the calculations in order to normalize gain differences between spectra. The same relationship holds for peak areas in \(^{31}\text{P} \) nmr spectra.

For the reaction of trimethyl phosphite with methyl iodide (determination of \( k_1 \)), a total of 15 spectra were obtained at intervals of 2000 sec between the first 6 spectra and 2500 sec between the remaining 9. Each spectra contains 15 pulses. The reaction was followed by observing the increase in the dimethyl methyl phosphonate peak with time; the relative height of the peak was determined by dividing the peak height by the peak height of the external standard, \((\text{MeO})_3\text{P(0)}\). The second order rate constant for methylation of trimethyl phosphite was obtained by dividing the slope of the plot of \( \ln\{RPH[(\text{MeO})_2\text{P(0)Me}]_{\text{inf}} - RPH[(\text{MeO})_2\text{P(0)Me}]_t \} \) vs. time by the methyl iodide concentration which remains essentially constant.

For the reaction of methyl diethylphosphinite with methyl iodide (determination of \( k_2 \)), 6 spectra were recorded at intervals ranging from 200 - 800 seconds. Each spectra consists of 3 pulses. The reaction was followed by observing the decrease in the diethylmethoxymethyl-
phosphonium iodide signal with time. From a spectra taken after the reaction was complete ([Et$_2$P(OMe)]$_{inf}$ = [Et$_2$POMe]$_o$), the concentration/unit factor was determined for the product (methyl diethyl phosphine oxide). This value was used to determine the concentration/unit factor for the phosphonium salt by subtraction ([Et$_2$P* (OMe)Me]$_t$ = [Et$_2$P(OMe)]$_{inf}$ - [Et$_2$P(OMe)]$_t$). The concentration of Et$_2$P*(OMe)Me was determined from the relative peak height for each spectra recorded during the experiment ([Et$_2$P*(OMe)Me] = RPH x M). The second order rate constant, k$_2$, was obtained as the slope of the plot of 1/[Et$_2$P*(OMe)Me]$_t$ vs. time.

For the autocatalytic reactions, between 6 and 15 spectra (taken at appropriate intervals ranging from 100 - 5000 seconds) were recorded depending upon the rate of the reaction. Each spectra consists of 3 pulses. The reactions were followed by observing the decrease in the phosphorus ester peak with time. Table 4.2 reports the observed $^{31}$P chemical shifts for the phosphorus esters, phosphonium salts, and products of the Arbuzov reactions studied. The relative height of the phosphorus ester peak was determined by dividing the height of the peak by the height of the phosphonium salt peak (whose concentration remains essentially constant throughout the experiment). The second order rate constants (k$_2$) were obtained by dividing the slope of the plot of ln[RPH(ABPOMe)] vs. time by the phosphonium ion concentration. For one run of the reaction
Table 4.2 Observed $^{31}$P chemical shifts$^a$

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>ABPOMe</th>
<th>ABP$(OMe)Me$</th>
<th>ABP$(O)Me$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>OMe</td>
<td>138</td>
<td>52</td>
<td>30</td>
</tr>
<tr>
<td>OMe</td>
<td>Ph</td>
<td>158</td>
<td>77</td>
<td>41</td>
</tr>
<tr>
<td>OMe</td>
<td>Et</td>
<td>185</td>
<td>96</td>
<td>55</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>112</td>
<td>72</td>
<td>26</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>137</td>
<td>102</td>
<td>44</td>
</tr>
</tbody>
</table>

$^a$ Chemical shifts reported are downfield from 85% $\text{H}_3\text{PO}_4$ for solutions in propylene carbonate and referenced to trimethylphosphate ($\delta = 1.9$ppm from 85% $\text{H}_3\text{PO}_4$).
of methyl diphenylphosphinite with diphenylmethoxymethylphosphonium triflate, where instrument resolution problems resulted in rather broad peaks, relative peak areas were used instead of heights.
References


53. Spears, L. G., Jr. unpublished results.


82. Reference 30, page 5.


95. Reference 2, page 57.


Appendix I

Conductivity and $^{31}$P nmr kinetic data
Figures 5.1 – 5.4 Conductivity kinetic results.

Phosphonium iodide concentration as a function of time for the reactions:

\[
\begin{align*}
\text{MeI} & \\
\text{ABPOMe} & \rightarrow \text{ABP(O)Me}
\end{align*}
\]

in propylene carbonate at 25.0 °C

In the following four figures, the circles represent experimental data points. The solid curve is that obtained by numerical integration of the rate law.
Figure 5.1 (MeO)$_3$P$^+$Me Concentration as a function of time for the reaction:

\[
\begin{align*}
\text{MeI} & \quad \text{(MeO)$_3$P} \\
& \quad \text{\rightarrow (MeO)$_2$P(O)Me}
\end{align*}
\]

$[(\text{MeO})_3\text{P}]_o = 0.7119$ molar

$[\text{MeI}]_o = 2.068$ molar
Figure 5.2  PhP⁺(OMe)₂Me Concentration as a function of time for the reaction:

\[
\begin{align*}
\text{PhP(OMe)₂} & \xrightarrow{\text{MeI}} \text{PhP(O)(OMe)Me} \\
[\text{PhP(OMe)₂}]_0 &= 0.07163 \text{ molar} \\
[\text{MeI}]_0 &= 0.3394 \text{ molar}
\end{align*}
\]
Figure 5.3 EtP\(^+\)(OMe)\(_2\)Me Concentration as a function of time for the reaction:

\[
\text{EtP(OMe)\(_2\) + MeI} \rightarrow \text{EtP\(^+\)(OMe)\(_2\)Me}
\]

\([\text{EtP(OMe)\(_2\)}]_0 = 0.05104 \text{ molar}\)

\([\text{MeI}]_0 = 0.08304 \text{ molar}\)
Figure 5.4 Et₂P⁺(OMe)Me Concentration as a function of time for the reaction:

\[
\begin{align*}
\text{MeI} & \\
\text{Et₂POMe} & \rightarrow \text{Et₂P(O)Me}
\end{align*}
\]

\[\text{[Et₂POMe]}_o = 0.0085 \text{ molar}\]
\[\text{[MeI]}_o = 0.02165 \text{ molar}\]

Every third data point up to 12000 seconds and every point thereafter is shown.
Figures 5.5 - 5.14 $^{31}$P nmr kinetic results

$^{31}$P nmr spectra and kinetic plots
Figure 5.5 $^{31}$P nmr spectra for the reaction:

$$\text{MeI} \quad (\text{MeO})_3\text{P} \xrightarrow{\text{in propylene carbonate at } 26.4 \, ^\circ\text{C}} (\text{MeO})_2\text{P(O)Me}$$

$[(\text{MeO})_3\text{P}]_0 = 0.3842 \text{ molar}$

$[\text{MeI}]_0 = 0.3932 \text{ molar}$
Figure 5.6 Kinetic plot for the reaction:

\[
\text{MeI} \\
\text{\((MeO)_3P\) } \rightarrow \text{\((MeO)_2P(O)Me\)}
\]

in propylene carbonate at 26.4 °C

\[\text{[(MeO)_3P]}_0 = 0.3842 \text{ molar}\]

\[\text{[MeI]}_0 = 0.3932 \text{ molar}\]

The circles represent experimental data points. The solid line is the least squares fit of these points.
Figures 5.7 $^{31}$P nmr spectra for the reaction:

$$(\text{MeO})_3\text{P} + \text{Me} \rightarrow (\text{OMe})_2\text{P(O)Me}$$

in propylene carbonate at 26.4 °C

$[(\text{MeO}_3\text{P})_0 = 0.2436 \text{ molar}]$

$[(\text{MeO}_3\text{P}^*\text{Me})_0 = 0.1055 \text{ molar}]$
Figure 5.8 Kinetic plot for the reaction

\[
\text{(MeO)}_3P + \text{Me} 
\rightarrow 
\text{(OMe)}_2P(0)\text{Me}
\]

in propylene carbonate at 26.4 °C

\[[\text{(OMe)}_3P]_0 = 0.2436 \text{ molar}\]

\[[\text{PhP}^+(\text{OMe})_2\text{Me}]_0 = 0.1055 \text{ molar}\]

The circles represent experimental data points. The solid line is the least squares fit of these points.
Figure 5.9 $^{31}$P nmr spectra for the reaction:

$$\text{Ph}_2\text{P}^+(\text{OMe})\text{Me} \rightarrow \text{Ph}_2\text{P(O)Me}$$

in propylene carbonate at 26.4 °C

[Ph$_2$POMe]$_o$ = 0.1729 molar

[Ph$_2$P$^+$ (OMe)Me]$_o$ = 0.1058 molar
Figure 5.10 Kinetic plot for the reaction

\[
\text{Ph}_2\text{P}^+\text{(OMe)Me} \xrightarrow{\text{Ph}_2\text{P(o)Me}} \text{Ph}_2\text{P(o)Me}
\]

in propylene carbonate at 26.4 °C

\[[\text{Ph}_2\text{POMe}]_0 = 0.1729 \text{ molar}\]

\[[\text{Ph}_2\text{P}^+(\text{OMe)Me}]_0 = 0.1058 \text{ molar}\]

The circles represent experimental data points. The solid line is the least squares fit of these points.
Figures 5.11 $^{31}$P nmr spectra for the reaction:

$$\text{EtP}^+(\text{OMe})_2\text{Me} \xrightarrow{} \text{EtP}(\text{O})(\text{OMe})\text{Me}$$

in propylene carbonate at 26.4 °C

$[\text{EtP}(\text{OMe})_2]_0 = 0.3316$ molar

$[\text{EtP}^+(\text{OMe})_2\text{Me}]_0 = 0.1810$ molar
Figure 5.12 Kinetic plot for the reaction:

\[ \text{EtP}^+(\text{OMe})_2\text{Me} \quad \text{EtP(MeO)}_2 \xrightarrow{\text{EtP}} \text{EtP(O)(MeO)Me} \]

in propylene carbonate at 26.4 °C

\[ [\text{EtP(MeO)}_2]_o = 0.3316 \text{ molar} \]

\[ [\text{EtP}^+(\text{OMe})_2\text{Me}]_o = 0.1810 \text{ molar} \]

The circles represent experimental data points. The solid line is the least squares fit of these points.
Figures 5.13 $^{31}P$ nmr spectra for the reaction:

$$\text{Et}_2\text{P}^+\text{(OMe)Me} \rightarrow \text{Et}_2\text{P(O)Me}$$

in propylene carbonate at 26.4 °C

$[\text{Et}_2\text{POMe}]_0 = 0.3789$ molar

$[\text{Et}_2\text{P}^+(\text{OMe})\text{Me}]_0 = 0.07163$ molar
Figure 5.14 Kinetic plot for the reaction

\[
\text{Et}_2\text{P}^+(\text{OMe})\text{Me} \xrightarrow{} \text{Et}_2\text{P(O)Me}
\]

in propylene carbonate at 26.4 °C

\[
[\text{Et}_2\text{POMe}]_0 = 0.3789 \text{ molar}
\]

\[
[\text{Et}_2\text{P}^+(\text{OMe})\text{Me}]_0 = 0.07163 \text{ molar}
\]

The circles represent experimental data points. The solid line is the least squares fit of these points.
Appendix II

Spectral data for the phosphonium salts:

Ph₂P⁺EtMe OTf⁻
Et₂P⁺PhMe OTf⁻
Et₃P⁺Me OTf⁻
Figure 6.1

$^1$H nmr of Ph$_2$P$^+$EtMe OTf$^-$
in CDCl$_3$ referenced to tetramethysilane

![NMR spectrum diagram with labeled peaks for Ph-P, CHCl$_3$, CH$_3$-CH$_2$-P, P-Me, and CH$_3$-CH$_2$-P]
Figure 6.2

$^1$H nmr of Et$_2$P·PhMe OTf$^-$

in CDCl$_3$ referenced to tetramethysilane
Figure 6.3

$^1\text{H} \text{ nmr of Et}_3\text{P}^+\text{Me OTf}^-$

in CDCl$_3$ referenced to tetramethylsilane
Table 6.1
High resolution mass spectrometry results
for the phosphonium salts:
$\text{ABP}^+\text{EtMe OTf}^-$

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>Observed ion</th>
<th>observed mass (amu)</th>
<th>expected mass (amu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>$\text{C}<em>{15}\text{H}</em>{18}\text{P}^+$</td>
<td>229.1148&lt;sup&gt;a&lt;/sup&gt;</td>
<td>229.114610</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>$\text{C}<em>{11}\text{H}</em>{18}\text{P}^+$</td>
<td>181.1146&lt;sup&gt;b&lt;/sup&gt;</td>
<td>181.114610</td>
</tr>
<tr>
<td>Et</td>
<td>Et</td>
<td>$\text{C}<em>7\text{H}</em>{18}\text{P}^+$</td>
<td>133.1147&lt;sup&gt;c&lt;/sup&gt;</td>
<td>133.114610</td>
</tr>
</tbody>
</table>

a. Reference precise mass used: 218.985600 amu.
b. Reference precise mass used: 168.988800 amu.
c. Reference precise mass used: 130.992000 amu.
Appendix III

"ARBUZOV" and "INTERP" programs
"ARBUZOV" Program

REAL MC
REAL SPCOND(100), SALT(100), MECOND(100)
INTEGER*4 TIMET(100), TIMEH(100), TIMEM(100), TIMES(100)
INTEGER TH, TM, TS, NOPTS, TIMEHO, TIMEMO, TIMESO
BYTE FILNAM(15), EXFILE(15)
WRITE(5,1)
1 FORMAT( 'FILENAME '*)
READ(5,5,FILNAM
5 FORMAT(15A1)
WRITE(5,15)
15 FORMAT( 'ENTER STARTING TIME IN HR., MIN., SEC.' )
READ(5,25,TIMEHO, TIMEMO, TIMESO)
25 FORMAT(I3, I3, I3)
WRITE(5,600)
600 FORMAT( 'ENTER FILENAME OF EXPERIMENTAL DATA: '*)
READ(5,601,EXFILE
601 FORMAT(15A1)
EXFILE(15)=0
OPEN(UNIT=2, NAME=EXFILE, DISP='SAVE', READONLY, TYPE='OLD')
L=1
500 READ(2, 400, END=401)MC, TH, TM, TS
400 FORMAT(E10.0, I3, I3, I3)
MECOND(L)=MC
TIMEH(L)=TH
TIMEM(L)=TM
TIMES(L)=TS
L=L+1
GO TO 500
401 NOPTS=L-1
I=1
35 SPCOND(I)=MECOND(I)*0.250
C ****FOLLOWING CALCULATION IS FOR MODEL SALT ET3P+ME I-
C SALT(I)=(SPCOND(I)-7.00742E-07)/2.56191E-02
C ****FOLLOWING CALCULATION IS FOR MODEL SALT ET2P+PHME I-
C SALT(I)=(SPCOND(I)-3.28866E-06)/2.48097E-02
C ****FOLLOWING CALCULATION IS FOR MODEL SALT PH2P+ETME I-
C SALT(I)=(SPCOND(I)-3.96821E-6)/2.95985E-02
C TIMES(I)=(TIMEH(I)-TIMEHO)*60+TIMEM(I)-TIMEMO)*60+
&TIMES(I)-TIMESO
I=I+1
IF(I.LE.NOPTS)GO TO 35
FILNAM(15)=0
OPEN(UNIT=1, NAME=FILNAM, DISP='SAVE', TYPE='NEW')
WRITE (5,16)FILNAM
WRITE (1,16)FILNAM
16 FORMAT (/////////// 'FILENAME: ',15A1/)
WRITE (5, 17) TIMEHO, TIMEMO, TIMESO
WRITE (1, 17) TIMEHO, TIMEMO, TIMESO

17 FORMAT (' STARTING TIME: ', I3, ': ', I3': ', I3)
65 FORMAT(///2X, 'TIME[SEC.]', 12X, 'SALT CONC.[M]')
WRITE(5, 50) EXFILE
WRITE(1, 50) EXFILE

50 FORMAT(/// 'EXPERIMENTAL DATA LOCATED IN FILE: ', 15A1)
WRITE (1, 65)
WRITE(5, 65)
DO 90 I=1, NOPTS
WRITE(1, 75) TIMET(I), SALT(I)
WRITE(5, 75) TIMET(I), SALT(I)

75 FORMAT(8X, I9, 7X, 6X, E11.4)
90 CONTINUE
CLOSE(UNIT=1)
CLOSE(UNIT=2)
GO TO 100

95 WRITE (5, *) 'OPEN ERROR'
100 STOP
END
"INTERP" Program

IMPLICIT INTEGER*4 (I-N)
BYTE EXFILE(16)
BYTE CAFILE(16)
DIMENSION IXPT(100), YPT(100), NXPT(100), FNYPT(100)
INTEGER*4 TOTSEC, TOTPTS, DESPTS
INTEGER*4 IXPT, NXPT
TYPE*, 'EXPERIMENTAL DATA FILE?'
ACCEPT 10, EXFILE
10 FORMAT (16A1)
TYPE*, 'INTERPOLATED POINTS FILE?'
ACCEPT 15, CAFILE
15 FORMAT (16A1)
EXFILE(16)=0
OPEN (UNIT=1, NAME=EXFILE, TYPE='OLD')
READ(1, 19, END=20) IXPT(J), YPT(J)
19 FORMAT(8X, 19, 13X, E11.4)
20 TOTPTS=J-1
TOTSEC=IXPT(J-1)
TYPE*, 'NUMBER OF EQUALLY SPACED POINTS DESIRED?'
ACCEPT*, DESPTS
INCR=TOTSEC/DESPTS
L=0
J=1
30 DO 40 I=INCR, TOTSEC, INCR
35 IF(IXPT(J).GT.1) GO TO 60
J=J+1
40 GO TO 30
50 IF(IXPT(J).LE.0) GO TO 60
J=J+1
55 GO TO 30
60 L=L+1
NXPT(L)=I
FNYPT(L)=YPT(J-1)+(I-IXPT(J-1))*(YPT(J)-YPT(J-1))/
& (IXPT(J)-IXPT(J-1))
40 CONTINUE
CAFILE(16)=0
OPEN (UNIT=2, NAME=CAFILE, DISP='SAVE', TYPE='NEW')
WRITE(2, 70) CAFILE
70 FORMAT(///,'FILENAME: ', 16A1)
WRITE(2, 80)
80 FORMAT(///, 10X, 'TIME[SEC. ]', 10X, 'CONC. [M]')
WRITE (2, 85)
85 FORMAT(12X, '0', 15X, '0.0000')
DO 90 I=1, L
WRITE(2,100) NXPT(I), FNYPT(I)
90 CONTINUE
CLOSE (UNIT=1)
CLOSE(UNIT=2)
STOP
END