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Gas-Phase Chemistry of Trimethyl Phosphite

David R. Anderson,[†] Charles H. DePuy,* Jonathan Filley, and Veronica M. Bierbaum

Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309. *Received April 9, 1984*

Abstract: The reactions of trimethyl phosphite, $(CH_3O)_3P$, with the nucleophiles H_2N^-, CH_3NH^-, $(CH_3)_2N^-$, HO^-, $H^{18}O^-$, CH_3O^-, CD_3O^-, H^-, F^-, H_2P^-, $CH_2{=}CH{-}CH_2^-$ and $(CH_3)_2C{=}C(CH_3)CH_2^-$ were investigated. Products, branching ratios, and reaction rate constants are reported. Reactions generally proceed through an ion-dipole complex $[Z^-{\cdot}(CH_3O)_3P]$, to a phosphoranide anion intermediate, $[(CH_3O)_3PZ^-]$, to displacement of methoxide to form a new ion-dipole complex $[CH_3O^-{\cdot}(CH_3O)_2PZ]$. If an additional acidic hydrogen is available on the nucleophile, the major products result from proton abstraction by methoxide: $[CH_3O^-{\cdot}(CH_3O)_2PYH] \rightarrow (CH_3O)_2PY^- + CH_3OH$. When the displacement of methoxide from phosphorus is sufficiently endothermic, a competing attack at carbon by the original nucleophile occurs: $[HY^-{\cdot}(CH_3O)_3P] \rightarrow CH_3YH + (CH_3O)_2PO^-$. Nucleophiles without an additional acidic hydrogen react similarly, but the final reaction products result from (1) S_N2 reaction of methoxide, $[(CH_3O)_2PZ{\cdot}CH_3O^-] \rightarrow Z(CH_3O)PO^- + CH_3OCH_3$, (2) S_N2 reaction of the original nucleophile, $[Z^-{\cdot}(CH_3O)_3P] \rightarrow CH_3Z + (CH_3O)_2PO^-$, (3) stabilization of the phosphoranide intermediate to give the adduct $Z(CH_3O)_3P^-$, and (4) expulsion of methoxide from the ion-dipole complex. Reaction mechanisms are discussed in terms of the nature of the nucleophiles, the observed products, and the thermodynamics of the displacement reaction.

Although the literature dealing with the chemistry of phosphorus compounds is vast, there are surprisingly few studies of the mechanisms by which lower valence organophosphorus compounds react. It is not difficult to suggest reasons why this is so. Many of the simplest compounds have unpleasant odors and are toxic. They may undergo multistep reactions which complicate kinetic analyses. Analytical techniques for separation and detection of the products are often lacking. Whatever the reasons in a particular case, kinetic and mechanistic data are sparse.

It seemed to us that this is an area in which gas-phase ion-molecule chemistry could make an important contribution. In a flowing afterglow apparatus, kinetic and mechanistic studies can be carried out on small samples and the products separated and analyzed in situ. Enough is known about the gas-phase chemistry of anions for us to feel confident that the results will apply as well to reactions in solution. In a previous paper we described the nucleophilic chemistry of H_2P^- and of some of the anions derived from it by ion-molecule reactions (e.g., PN_2^-, PCO^-, PS^-).[1] It is, however, in its role as an electrophile in such molecules as esters and amides that phosphorus is important in biological and ecological systems.[2,3]

Trimethyl phosphite, $(CH_3O)_3P$, seemed like an ideal substrate for these studies, because it offers the opportunity to compare nucleophilic attack on carbon and phosphorus in the same molecule. Its high volatility and ready availability also were considerations. Nucleophilic displacement reactions of alkoxy groups from phosphite esters occur in, for example, their reactions with Grignard and other organometallic reagents[2,4] but, except for a tracer and kinetic study with water,[5] do not appear to have been investigated in detail. More information is available for compounds with better leaving groups (for example, R_2PCl, etc.), but even in these cases knowledge is limited.

In the study reported in this paper we have examined the reactions of trimethyl phosphite with a number of nucleophiles at room temperature. We hoped to gain insight into the mechanism of displacement on phosphorus and were especially interested in the question of whether nucleophilic attack occurs by way of a proposed[6,7] tetracoordinate anionic intermediate, similar to the pentacoordinate anionic intermediate in reactions of silicon,[8,9] or whether phosphorus resembles carbon in reacting through an S_N2-like transition state. In addition we felt we could gain information about relative bond strengths to phosphorus; only approximate values are known for many important P-X bond dissociation energies.[2] In favorable cases the observation that a reaction occurs in the gas phase can place limits on bond dissociation energies.

Our current study examines the reactions of trimethyl phosphite with the nucleophiles H_2N^-, CH_3NH^-, $(CH_3)_2N^-$, HO^-, $H^{18}O^-$, CH_3O^-, CD_3O^-, H^-, F^-, H_2P^-, $CH_2{=}CH{-}CH_2^-$, and $(CH_3)_2C{=}C(CH_3)CH_2^-$. We find that the predominant reaction is a reversible nucleophilic attack at phosphorus, displacing methoxide anion. The displaced methoxide usually undergoes further reaction with the neutral product, either abstraction of an acidic hydrogen, if available, or nucleophilic attack at carbon. However, when the displacement at phosphorus by the original nucleophile is sufficiently endothermic, a competing attack by that nucleophile on the methyl carbon occurs, displacing the dimethyl phosphite anion. We also observe stable phosphoranide products ($(CH_3O)_3PZ^-$) in some of these reactions.

Only a few gas-phase ion studies of phosphorus compounds have been reported previously. Beauchamp and co-workers have measured the proton affinities of a number of phosphite, phosphate, and phosphorothionate esters.[10,11] They[12,13] and others[14,15] have also studied nucleophilic reactions of anions with phosphate and a few other phosphoryl compounds in the gas phase. Only a single report of nucleophilic reactions of anions with a tervalent phosphorus compound, PF_3, has appeared.[13]

[†] Present Address: Department of Chemistry, University of Colorado, Colorado Springs, Colorado 80933.

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Experimental Section

These experiments were performed at 298 K in a flowing afterglow system which has been described previously.[16] H_2N^-, CH_3NH^-, F^-, and H^- were formed by electron impact on NH_3, CH_3NH_2, NF_3, and CH_4, respectively. HO^- was generated by dissociative electron attachment to N_2O to form O^-, followed by hydrogen abstraction from CH_4. CH_3O^- and CD_3O^- were formed by an elimination reaction of H_2N^- with 1,2-dimethoxyethane and perdeuterio-1,2-dimethoxyethane, respectively. $(CH_3)_2N^-$, H_2P^-, $CH_2{=}CH{-}CH_2^-$, and $(CH_3)_2C{=}C(CH_3)CH_2^-$ were produced by proton abstraction with H_2N^- from their corresponding neutral acids. The amide ions were usually contaminated with small amounts of hydroxide ion due to reaction with adventitious water. However, products and branching ratios of the reactions between the amide ions and trimethyl phosphite were easily corrected by subtracting the contribution from reactions of hydroxide ion with trimethyl phosphite.

The selected ion flow tube (SIFT) technique[17] was employed for generation of $H^{18}O^-$ from $H_2{}^{18}O$. It was possible to generate $H^{18}O^-$ more cleanly in the SIFT than in the conventional flowing afterglow apparatus.

Helium pressures and flow rates ranged from 0.3 to 0.5 torr and 140 to 240 STP $cm^3\ s^{-1}$, respectively. Neutral reactant flow rates were determined by monitoring the pressure increase in a calibrated volume. Rate constants were determined by following reactant ion counts as a function of reaction distance. Measurements were made at several neutral flow rates and helium pressures, and the reported values are averages of four determinations. The experimental precision of each rate constant is better than ±10%; the overall accuracy of the rate constants is estimated to be ±25%. Branching ratios were determined in the manner described in reference 1. Mass discrimination in the detection system and the accuracy of branching ratios are discussed below.

In these studies the identities of the ion products were determined primarily from their mass-to-charge ratios. In cases where more than one possible structure could account for the observed mass-to-charge ratio, isotopic labeling allowed a more definitive identification (see Results section). Also, since neutral products were not detected, their identities were inferred from knowledge of the reactants and the observed product ions.

An unusual and as yet unexplained phenomenon occurred in the detection of ion products from the reactions of trimethyl phosphite. Generally in flowing afterglow experiments the total ion intensity is conserved throughout a reaction; that is, reactant ions are efficiently converted to product ions and the total ion count remains constant within experimental error (±10%). Some deviation from this conservation can result if product ions have greatly different diffusion coefficients than reactant ions or if quadrupole mass discrimination is substantial. However, in the trimethyl phosphite reactions 70–90% of the ion signal was lost upon complete conversion of reactant ions into product ions. This phenomenon was observed with all of the phosphorus-containing anions in this study and was made even more surprising by the fact that no such loss of signal occurred in our previous study with phosphide ion reactions.[1] Changes in diffusion coefficients would have the opposite effect, one of increasing the total ion intensity since the larger product ions would have lower diffusive loss rates. Discrimination against higher mass ions by the quadrupole mass filter was minimized by adjusting the resolution until no further change was observed in the ratio of a high-mass ion to a low-mass ion, and signal loss was not observed for non-phosphorus-containing ions.

The problem was traced to an inefficiency in the detection of these ions by the continuous channel electron multiplier (Murata Ceratron-E). To verify that in reality the ion intensity was conserved and that our branching ratios were accurate, direct measurements were made, using the reactions of amide and fluoride, of the ion currents on a Faraday plate at the entrance to the electron multiplier. Total ion flux remained constant throughout each reaction, and the branching ratios measured in this way were identical with those measured by using the electron multiplier. The reactions in this study for which a quantitative problem exists are those that generate both methoxide and phosphorus-containing ion products, since methoxide suffers from no detection inefficiency whereas the phosphorus-containing products do. Branching ratios were corrected for this effect.

All gases were obtained from commercial suppliers and were of the following purities: He (99.995%), NH_3 (99.999%), N_2O (99.99%), CH_4 (99.99%), CH_3NH_2 (98%), $(CH_3)_2NH$ (99%), NF_3 (99.8%), PH_3 (99.999%), and propene (99.0%). Trimethyl phosphite (Alfa Products) was distilled from sodium, stored over sodium, and then distilled directly into the flowing afterglow apparatus. Perdeuterio-1,2-dimethoxyethane (99+ atom % D) was obtained from MSD Isotopes and used without further purification. All other liquid reagents were distilled before use.

Results

The reactions between anions and trimethyl phosphite can be divided into two categories depending on whether or not the anion has an acidic hydrogen.

A. Anions with an Acidic Hydrogen. In most cases these anions react with trimethyl phosphite by addition and loss of methanol, as exemplified by the reaction of methylamide ion (eq 1). Amide

$$CH_3NH^- + (CH_3O)_3P \rightarrow (CH_3O)_2PNCH_3^- + CH_3OH \qquad (1)$$

ion itself reacts, in the main, analogously (eq 2a), but, in addition, a small amount of an M – 1 ion is formed by proton transfer (eq 2b) (branching ratios given over arrows). Amide ion reacts with

$$\begin{aligned} H_2N^- + (CH_3O)_3P &\xrightarrow[a]{0.9} (CH_3O)_2PNH^- + CH_3OH \\ &\xrightarrow[b]{0.1} (CH_3O)_2POCH_2^- + NH_3 \qquad (2) \end{aligned}$$

trimethyl phosphite with a rate constant of 2.8×10^{-9} cm^3 $molecule^{-1}$ s^{-1}, which is the same as the collision rate constant calculated by the ADO theory of Su and Bowers.[18]

Hydroxide ion forms the dimethyl phosphite ion at a similarly rapid rate ($k = 2.7 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}); this ion could, in principle, be formed either by attack on phosphorus followed by proton transfer or by S_N2 displacement on one of the methyl groups. An isotopic labeling experiment, in which $H^{18}O^-$ was formed in an external ion source, separated in a quadrupole mass filter and injected into the flow tube (the selected ion flow tube (SIFT) technique), showed that the former pathway actually occurs (eq 3).

$$H^{18}O^- + (CH_3O)_3P \rightarrow (CH_3O)_2P^{18}O^- + CH_3OH \qquad (3)$$

Hydride ion also reacts with trimethyl phosphite exclusively by addition and loss of methanol (eq 4), $k = 5.9 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}, to form the dimethoxyphosphide ion.

$$H^- + (CH_3O)_3P \rightarrow (CH_3O)_2P^- + CH_3OH \qquad (4)$$

In contrast to these highly reactive ions, the allyl and substituted allyl anions react much more slowly, and S_N2 displacement on carbon competes with attack on phosphorus (eq 5). The phosphide

$$\begin{aligned} CH_2{=}CH{-}CH_2^- + (CH_3O)_3P &\xrightarrow[a]{0.8} (CH_3O)_2P{-}CH{\cdots}CH{\cdots}CH_2^- + CH_3OH \\ &\xrightarrow[b]{0.2} (CH_3O)_2PO^- + CH_3CH_2CH{=}CH_2 \qquad (5) \end{aligned}$$

anion reacts exclusively, but very slowly, by displacement on methyl.

B. Anions without an Acidic Hydrogen. Methoxide ion forms two ionic products with trimethyl phosphite, the dimethyl phosphite ion (eq 6a) and an adduct (eq 6b). More details of this reaction

$$\begin{aligned} CH_3O^- + (CH_3O)_3P &\xrightarrow[a]{0.52} (CH_3O)_2PO^- + CH_3OCH_3 \\ &\xrightarrow[b]{0.48} (CH_3O)_4P^- \qquad (6) \end{aligned}$$

are revealed with trideuteriomethoxide ion, which forms the primary products shown in eq 7 as well as a number of secondary

$$\begin{aligned} CD_3O^- + (CH_3O)_3P &\xrightarrow[a]{0.37} CH_3O^- + (CH_3O)_2POCD_3 \\ &\xrightarrow[b]{0.17} (CH_3O)_2PO^- + CH_3OCD_3 \\ &\xrightarrow[c]{0.16} CD_3O(CH_3O)PO^- + CH_3OCH_3 \\ &\xrightarrow[d]{0.30} (CH_3O)_3POCD_3^- \qquad (7) \end{aligned}$$

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Table I. Products, Branching Ratios, Rate Constants, and Efficiencies of Reactions of Trimethyl Phosphite

anion	products	I_x/I_T[a]	k_{exptl}[b]	k_{exptl}/k_{ADO}[c]
CH_3NH^-	$(CH_3O)_2PNCH_3^- + CH_3OH$	1.0		
H^-	$(CH_3O)_2P^- + CH_3OH$	1.0	5.9×10^{-9}	0.55
H_2N^-	$(CH_3O)_2PNH^- + CH_3OH$	0.9	2.8×10^{-9}	1.0
	$(CH_3O)_2POCH_2^- + NH_3$	0.1		
HO^-	$(CH_3O)_2PO^- + CH_3OH$	1.0	2.7×10^{-9}	0.97
$CH_2{=}CH{-}CH_2^-$	$(CH_3O)_2PCHCH{=}CH_2^- + CH_3OH$	0.8[d]		
	$(CH_3O)_2PO^- + CH_3CH_2CH{=}CH_2$	0.2[d]		
$(CH_3)_2C{=}C(CH_3)CH_2^-$	$(CH_3O)_2PCH(CH_3)C{=}C(CH_3)_2^- + CH_3OH$	0.7	$\leq 4 \times 10^{-11}$	≤0.03
	$(CH_3O)_2PO^- + (CH_3)_2C{=}C(CH_3)CH_2CH_3$	0.3		
H_2P^-	$(CH_3O)_2PO^- + CH_3PH_2$	1.0	$\leq 10^{-12}$	≤0.001
CH_3O^-	$(CH_3O)_2PO^- + CH_3OCH_3$	0.5[e]	1.6×10^{-9}	0.76
	$(CH_3O)_4P^-$	0.5[e]		
CD_3O^-	$CH_3O^- + (CH_3O)_2POCD_3$	0.37[f]	2.7×10^{-9}	1.2
	$(CH_3O)_2PO^- + CH_3OCD_3$	0.17[f]		
	$CD_3O(CH_3O)PO^- + CH_3OCH_3$	0.16[f]		
	$(CH_3O)_3POCD_3^-$	0.30[f]		
$(CH_3)_2N^-$	$CH_3O^- + (CH_3O)_2PN(CH_3)_2$	0.3[d]		
	$(CH_3O)_2PO^- + (CH_3)_3N$	0.6[d]		
	$(CH_3)_2N(CH_3O)PO^- + CH_3OCH_3$ or $(CH_3O)_2PNCH_3^- + CH_3OCH_3$	0.1[d]		
F^-	$(CH_3O)_2PO^- + CH_3F$	0.85	2.2×10^{-9}	0.83
	$F(CH_3O)PO^- + CH_3OCH_3$	0.10		
	$(CH_3O)_3PF^-$	0.05		

[a] Branching ratio; where adduct is formed the branching ratios will depend on He pressure. [b] In $cm^3\ molecule^{-1}\ s^{-1}$. [c] Efficiency. [d] Estimated at a single flow of trimethyl phosphite. [e] Calculated from CD_3O^- data. [f] Corrected for signal loss in detection of phosphorus-containing products.

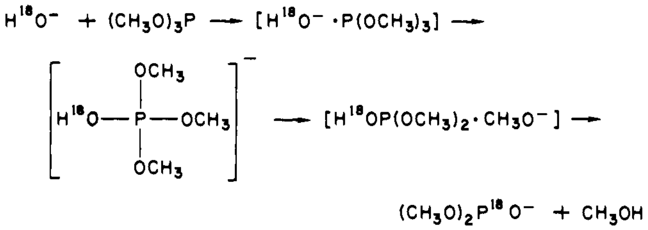
products. The nature and origin of these products will be considered in the Discussion section.

An analogous series of ions is produced by dimethylamide and fluoride ions. Products, branching ratios, rate constants (where measured), and reaction efficiencies for all the reactions studied are collected in Table I.

C. Gas-Phase Acidity of $(CH_3O)_2POH$ and $(CH_3O)_2PNH_2$. These acidities were determined by a bracketing technique in which the anions ($(CH_3O)_2PO^-$ and $(CH_3O)_2PNH^-$ from reaction of $(CH_3O)_3P$ with HO^- and H_2N^-, respectively) were allowed to react with neutral acids of known gas-phase acidity. Since dimethyl phosphite reacts readily with H_2S but only very slowly with CH_3SH, its acidity can be bracketed as 357 ± 3 kcal/mol. The phosphoramidite ion reacts with PH_3 but not ethanol, giving an acidity of 373 ± 3 kcal/mol.

Discussion

With most anions studied our results are best interpreted as initial attack on phosphorus and displacement of methoxide:



$$H^{18}O^- + (CH_3O)_3P \longrightarrow [H^{18}O^- \cdot P(OCH_3)_3] \longrightarrow \left[H^{18}O-\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{P}}-OCH_3 \right]^- \longrightarrow [H^{18}OP(OCH_3)_2 \cdot CH_3O^-] \longrightarrow (CH_3O)_2P^{18}O^- + CH_3OH$$

As in most ion–molecule reactions the ion and neutral are attracted to one another by ion–dipole and ion–induced dipole forces until they enter a reaction complex which contains up to 20 kcal/mol of complexation energy. Approximately this same amount of energy is required to separate the products or must be removed to observe a stable adduct. Within this relatively long-lived complex, reactions may occur provided their activation energies are less than the complexation energy. The products of the reaction remain within a similar complex long enough that further reactions are often observed. For example, the product complex in the above reaction lives long enough for an exothermic proton transfer to occur, and only the more stable anion, the dimethyl phosphite ion, emerges as a product.

Amide and methylamide react similarly, but the former is a strong enough base ($\Delta H°_{acid}(NH_3)$ = 404 kcal/mol) to remove a proton to form an M − 1 ion. The structure of this ion is unknown; it may simply be the ion resulting from loss of a proton from the methyl group and stabilized by dipolar forces[19] or it may be a rearranged ion of, for example, the structure

$$(CH_3O)_2P({=}O){-}CH_2^-$$

Although at first glance hydride ion appears to form an unexpected product, it too reacts analogously, if one considers it to be a proton attached to a nucleophilic electron pair, viz:

$$H^- + (CH_3O)_3P \rightarrow [H{-}P(OCH_3)_2{\cdot}CH_3O^-] \rightarrow (CH_3O)_2P^- + CH_3OH$$

The allyl anion and the hydroxide ion have almost identical basicities, yet, in contrast to the hydroxide ion, the allyl and trimethylallyl anions react slowly and give significant amounts of displacement on carbon. The phosphide ion also reacts extremely slowly. These results can be understood if they are considered in light of the thermodynamic data given in Table II.[20-23] Because of the great strength of the phosphorus–oxygen bond the initial displacement of methoxide by all the anions is expected to be endothermic or at best thermoneutral. The overall reaction is driven to completion by the strongly exothermic proton-transfer step which follows. Because the phosphorus–carbon bond is so much weaker than the phosphorus–oxygen bond, reaction of the allyl anion with trimethyl phosphite to form methoxide ion should be quite endothermic and hence can reasonably

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Table II. Enthalpies and Relative Product Yields from the Reactions of Trimethyl Phosphite

anion (X^-)	$\Delta H°_{diss}$(P–X), kcal/mol	EA(X·), kcal/mol	$\Delta H(S_N2\text{-}P)$,[a] kcal/mol	products from attack at: phosphorus	carbon
CH_3NH^-	~74[b]	~11[c]	~-2	1.0	0
H^-	78[d]	17[e]	0	1.0	0
H_2N^-	~74[b]	17[f]	~4	1.0	0
HO^-	97[d]	42[f]	6	1.0	0
$CH_2{=}CH{-}CH_2^-$	~50[g]	8[h]	~19	0.8	0.2
$(CH_3)_2C{=}C(CH_3)CH_2^-$	~50[g]	~8[i]	~19	0.7	0.3
H_2P^-	50[d]	29[f]	40	0	1.0
CD_3O^-	97[d]	36[f]	0	1.0[j]	0
$(CH_3)_2N^-$	~74[b]	~13[c]	~0	1.0[j]	0
F^-	117[d]	78[f]	22	0.1	0.9

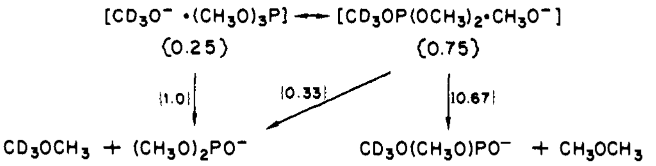
[a] Enthalpy for the displacement of methoxide: $\Delta H = \Delta H°_{diss}(P\text{–}O) - \Delta H°_{diss}(P\text{–}X) + EA(X\cdot) - EA(CH_3O\cdot)$; $\Delta H°_{diss}(P\text{–}O) = 97$ kcal/mol (ref 2), $EA(CH_3O\cdot) = 36.4$ kcal/mol (ref 20). [b] This work; see text. [c] Reference 22. [d] Reference 2. [e] Reference 21. [f] Reference 20. [g] Estimated by subtracting the average difference between CH_3–X and allyl–X bond enthalpies from the known CH_3–P bond enthalpy. [h] Reference 23. [i] Estimated to be similar to that for allyl. [j] For those anions which lack an acidic hydrogen and for which displacement at phosphorus is thermoneutral, it is concluded that attack at phosphorus (with equilibration of the ligands) precedes displacement at carbon; see text.

be expected to be slow. When displacement on phosphorus becomes difficult a competing displacement on carbon is revealed. The phosphorus–phosphorus bond is so weak that displacement on phosphorus by phosphide probably does not occur at all. The phosphide ion is known to undergo gas-phase displacement reactions only slowly.[1]

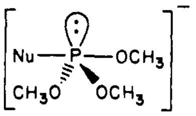
Accurate bond dissociation enthalpy values for P–X bonds are sparse;[2] for example, $\Delta H°_{diss}$ for the P–N bond is not known. The fact that dimethylamide displaces methoxide from trimethyl phosphite allows us to estimate that $\Delta H°_{diss} \geq 74$ kcal/mol for the P–N bond in the product. If we assume $\Delta H° = 0$ for the reaction, this value can be calculated from the P–O bond strength and the electron affinities of CH_3O and $(CH_3)_2N$ (Table II).

Additional facets of nucleophilic reactions on trimethyl phosphite are revealed by the results with CH_3O^- and CD_3O^-. The results using the unlabeled methoxide appear simple, with only two products being formed, the dimethyl phosphite ion formed by S_N2 displacement on carbon and the tetramethoxyphosphoranyl anion formed by addition and subsequent loss of energy to the bath gas. When the deuterium-labeled methoxide ion is used, however, the complexity of the process becomes evident. In addition to four primary products, a number of secondary products are formed. Primary and secondary products are identified by studying product ion ratios as a function of trimethyl phosphite flows as shown in Figure 1. By extrapolation to zero flow the branching ratios for the initial products can be identified (Table I).

The first conclusion to be drawn is that there is complete equilibration within a complex among the various methoxyl groups before displacement on a methyl carbon occurs. This conclusion is based on the fact that deuterated and undeuterated dimethyl phosphite ions are formed in equal amounts. This is the expected result for complete equilibration since the ratio of complexes with CH_3O^- to those with CD_3O^- is three to one, the latter can form only undeuterated phosphite and the former can form a two to one ratio of deuterated to undeuterated phosphite, assuming no isotope effects.



Additional information about the reaction mechanism and the structure of the ions can be gained by consideration of the secondary products of this reaction. A key question is that regarding the nature of the tetracoordinate anion



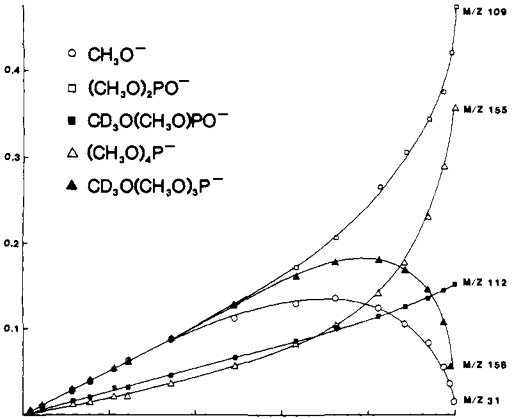


Figure 1. Relative intensity of product ions (I_x) vs. relative conversion of reactant CD_3O^- (ΔI_{34}) for the reaction of CD_3O^- with trimethyl phosphite (0.3 torr He, 298 K).

Is it an intermediate or a transition state? An approach to the answer is attainable since we have some indication of the structure of this species after it has been stabilized by collision with the helium buffer gas. Two possible structures are (1) a stabilized ion–dipole complex, with the methoxide ion held in the vicinity of trimethyl phosphite by ion–dipole forces or (2) a covalently bonded pentavalent anion: $CH_3O^-\cdot P(OCH_3)_3$ or $(CH_3O)_4P^-$. As can be seen from Figure 1, an important secondary reaction is one in which methoxide is transferred from the tetramethoxy anion to trimethyl phosphite

$$\underset{m/z\ 158}{[CD_3OP(OCH_3)_3]^-} + (CH_3O)_3P \rightarrow \underset{m/z\ 155}{[(CH_3O)_4P]^-} + CD_3OP(OCH_3)_2$$

Let us suppose that the stabilized phosphorus anion is simply a cluster; that is, after cooling to room temperature one methyl group differs from the other three. Then, since we know that complete equilibration of the methoxyls occurs before stabilization, the stabilized clusters will consist of 25% $CD_3O^-\cdot P(OCH_3)_3$ and 75% $CH_3O^-\cdot P(OCD_3)(OCH_3)_2$. The former ion will always transfer CD_3O^- to another trimethyl phosphite molecule, and hence an ion of *m/z* 158 should persist in the spectrum even at very high flows of trimethyl phosphite where there is time for several transfers to take place. On the other hand if the ion is symmetrical, or if there is rapid equilibration of the methoxyl groups even at room temperature, then methoxyl transfer will be three times more likely than deuteriomethoxyl transfer at each collision and the *m/z* 158 peak will rapidly disappear with increasing trimethyl phosphite flows. This is indeed what happens and demonstrates the equivalency of the methoxyls in the tetracoordinate anions.

Conclusion

Trimethyl phosphite reacts readily with a variety of nucleophiles in the gas phase. Initial reaction proceeds through formation of an ion–dipole complex to a tetracoordinate phosphoranide intermediate and then to a new ion–dipole complex consisting of the displaced methoxide and the newly-formed neutral. In cases where subsequent reactions are fairly slow, collisional stabilization of the phosphoranide intermediate is possible, and this adduct is observed. If the original nucleophile contains a hydrogen which is labile in the intermediate, then abstraction of this hydrogen by methoxide is the preferred final step in the reaction. When the displacement of methoxide is sufficiently endothermic a competing S_N2 reaction at a methyl carbon by the original nucleophile occurs.

Nucleophiles without an additional labile proton react similarly, but now a more equal competition is established between S_N2 reactions at carbon by the original nucleophile and the displaced methoxide. In addition to products formed by both of these reactions, the relative amounts of which are strongly dependent on the thermodynamics of the ion–dipole complex equilibrium, both methoxide ion and the phosphoranide adduct are now observed.

These results should be applicable to gas-phase electrophilic reactions of tervalent phosphorus in general. We have also examined reactions, similar to those reported here, with triisopropyl phosphite. The results are comparable; the only major difference comes about due to the possibility of elimination of propene from reaction of a strong base with an isopropyloxy group. We intend to continue studying the reactions of phosphorus in the gas phase.

Acknowledgment. We gratefully acknowledge the support of this work by the U.S. Army Research Office under Contract DAAG29-82-K-0025. We thank Jane Van Doren for her assistance in the SIFT studies.

Registry No. $(CH_3O)_3P$, 121-45-9; CH_3NH^-, 54448-39-4; H^-, 12184-88-2; H_2N^-, 17655-31-1; HO^-, 14280-30-9; $CH_2{=}CHCH_2^-$, 1724-46-5; $(CH_3)_2C{=}C(CH_3)CH_2^-$, 91760-20-2; H_2P^-, 22569-71-7; CH_3O^-, 3315-60-4; CP_3O^-, 51679-31-3; $(CH_3)_2N^-$, 34285-60-4; F^-, 16984-48-8; $(CH_3O)_2POH$, 96-36-6; $(CH_3O)_2PNH_2$, 39230-41-6.

Chiroptical Properties of Disulfides. Ab Initio Studies of Dihydrogen Disulfide and Dimethyl Disulfide

Arvi Rauk

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4.
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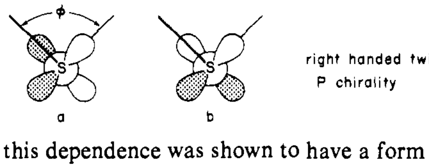
Abstract: The ground- and excited-state electronic structures of H_2S_2 and $(CH_3)_2S_2$ have been investigated as a function of the S–S dihedral angle, ϕ, by using ab initio SCF and CI calculations with a large basis set. The SCF energies for H_2S_2 and $(CH_3)_2S_2$, −796.23280 and −874.24551 hartrees, respectively, are lower than has hitherto been achieved. The cis and trans barriers to hindered rigid rotation are 37.7 and 21.7 kJ/mol, respectively. Equilibrium dihedral angles of 91.3° and 86.5° are interpolated for the two systems. Ionization potentials are calculated to second order in many-body perturbation theory. The nature of the lowest excited singlet state is found to be in accord with predictions based on Bergson's model of the disulfide linkage at all values of ϕ. However, the second and higher excited states change character significantly as a result of avoided crossings of states in the vicinity of $\phi = 70°$ and 120°. Optical rotatory strengths and oscillator strengths are calculated at several values of ϕ, and the relationship to experimental spectroscopic studies on both cyclic and acyclic disulfides is discussed. For the latter compounds, it is found that the rotatory strengths of the two degenerate transitions at the equilibrium geometry, $\phi \simeq 90°$, do not cancel.

In part because of the importance of the disulfide link to the tertiary structures of proteins, considerable experimental and theoretical efforts have been expended in the investigation of molecules which contain the –S—S– unit. The chemical, physical, and spectroscopic properties of disulfides are intimately linked to the torsional dihedral angle, ϕ, which relates the two RSS planes. The Bergson model[1] of the disulfide unit offers a qualitative explanation of many of the properties of disulfides which exhibit a strong dependence on the value of ϕ. Bergson assumed that only the energies of the two highest occupied molecular orbitals (MO's), which consist of the symmetric and antisymmetric combinations of the nonbonding 3p orbitals of sulfur, will show a strong dependence on ϕ. With use of simple overlap considerations, this dependence was shown to have a form very similar to that shown for the MO's, 9a and 8b, in Figure 1. The energetic behavior of the highest occupied MO's immediately suggests an explanation for the twofold rotation barrier and the equilibrium torsion angle of approximately 90°, as well as the observed ϕ dependence of the lowest ionization potential. If one postulates that the lowest excited state of the disulfide chromophore originates from an electronic excitation out of the highest occupied MO into an orbital such as $\sigma_{SS}{}^*$ which does not have a strong ϕ dependence, then the red shift observed for the lowest band in the UV spectrum of simple disulfides as ϕ is distorted from 90° is also explained. Linderberg and Michl[2] have used Bergson's model and have employed semiempirical MO/CI calculations to explain the inherent lack of optical activity of the first transition in acyclic disulfides and the strong angle dependence of the sign of the rotatory strength. They predicted that for a disulfide link with a right-handed twist (P chirality), the sign of the optical activity of the lowest transition is positive if the torsion angle, ϕ, is less than 90° and negative for $\phi > 90°$. According to the Bergson model,[1] the change in sign occurs as the result of the crossing of two electronic states of A and B symmetry to which the rotatory strengths of the transitions are oppositely signed. The accidential degeneracy of the two states and the near cancellation of rotatory strengths



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(1) Bergson, G. *Ark Kemi* **1958**, *12*, 233–237; **1962**, *18*, 409–434.

(2) Linderberg, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 2619–2625.