Trimethylphosphine: Anion–Molecule Reactions and Acidity in the Gas Phase

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Gas-phase acidity of trimethylphosphine has been investigated at ambient temperature by examining proton-transfer reactions in 40 Pa of helium buffer gas in a Flowing Afterglow instrument. On the basis of the occurrence–non-occurrence of a number of proton-transfer reactions and the observation of rapid H–D exchange between D_2O and the conjugate base of trimethylphosphine, it has been determined that trimethylphosphine is more acidic than water. Quantitative measurements are reported for the reaction of trimethylphosphine with atomic oxygen anion and methoxide. These latter two anions exhibit multiple reaction pathways, one of which is proton transfer. From measurements of the rate coefficients of these two reactions and the relative product yields, it is concluded that the gas-phase acidity of trimethylphosphine is very similar to that of the hydroxyl radical; the recommended value is $\Delta G^{\circ}_{acid}(PMe_3)$ 1 577 ± 13 kJ mol^{-1}. The derived acidity measurement is in slight contrast to recent theoretical and experimental estimates. Furthermore, it is found that anions which react only slowly with trimethylphosphine by proton transfer can undergo an alternative reaction which corresponds to addition of the neucleophilic anion to trimethylphosphine followed by loss of methane.

There is widespread interest in understanding the fundamental behaviour of organic compounds of sulphur, phosphorus, and silicon. This is due in part to their significance in bio-organic chemistry,[1] the semiconductor industry, and their relationship to the more traditionally studied oxygen, nitrogen, and carbon analogues. One aspect of recent interest has focused on the reactions of gas-phase anions with simple compounds containing these elements. Gas-phase techniques offer unique advantages in the study of reactive charged species, particularly the ability to eliminate solvation phenomena, aggregation, and ion-pairing effects. Various workers have utilized different gas-phase techniques to examine a few of the simple compounds of sulphur, phosphorus,[2] and silicon.

From such investigations, we now understand that whereas methyl chloride undergoes gas-phase anionic displacement reactions by the familiar displacement process, trimethylsilyl chloride reacts with the same anions by an addition–elimination process.[3] Other studies have shown that while dimethyl ether is non-acidic to the point where its conjugate base has not yet been experimentally studied,[4] dimethyl sulphide will give up a proton to the readily available, albeit strong, gas-phase bases amide and hydroxide.[5,6] Neither dimethyl ether[7] nor dimethyl sulphide[3,6,8] undergo a displacement process under room temperature energy conditions in the gas phase.

As part of their interest in MeX compounds, Ingemann and Nibbering recently examined the gas-phase acidity of trimethylphosphine, PMe_3, with the use of Fourier transform ion cyclotron resonance mass spectrometry.[6] Whereas trimethylamine cannot be deprotonated at ambient energies, Ingemann and Nibbering found that NH_2^-, $EtNH^-$, Me_2N^-, $Et(Me)N^-$, and $MeSCH_2^-$ ions react 'exclusively and irreversibly' with PMe_3 by proton transfer.[6] Successful measurement of the equilibrium constant in the HO^-–H_2O–PMe_3 system led Ingemann and Nibbering[6] to the conclusion of $\Delta G^{\circ}_{acid}(PMe_3)$ 1 606 ± 8 kJ mol^{-1} relative to $\Delta G^{\circ}_{acid}[H_2O]$ 1 607 ± 4 kJ mol^{-1}.

The gas-phase acidity value of trimethylphosphine obtained by Ingemann and Nibbering[6] compares favourably with recent *ab initio* calculations on the proton affinities of α-substituted methyl anions.[9] These calculations indicate that $^-CH_2PH_2$ is 96 kJ mol^{-1} weaker as a base than Me^-. Using the currently accepted value for the gas-phase acidity of methane of $\Delta G^{\circ}_{acid}(CH_4)$ 1 709 ± 5 kJ mol^{-1}, the *ab initio* calculations indicate that the hydrogen on carbon in methylphosphine should have an absolute gas-phase acidity of *ca.* 1 613 kJ mol^{-1}. Further, substitution of the remaining two phosphino hydrogens for methyls should serve to increase the acidity even more, such that $\Delta G^{\circ}_{acid}(PMe_3)$ can be expected to be less than the value derived for $MePH_2$. For example, propan-2-ol is 22 kJ mol^{-1} more acidic than methanol. Thus there appears to be reasonable agreement between the ion cyclotron resonance (I.C.R.) data[6] and the *ab initio*[9] calculations.

While we were carrying out gas-phase flowing afterglow experiments aimed at gaining insight into the utility of the atomic oxygen anion as a chemical ionization reagent,[10] we found that the atomic oxygen anion, $O^{-\bullet}$, reacted with trimethylphosphine to a significant degree by proton transfer (and to a much lesser degree by H_2^+ transfer which was the pathway of interest).[11] Since, in the gas phase, hydroxyl radical is well known to be significantly more acidic than water[12] (by 33 kJ mol^{-1}), and because reasonably endoergic reactions are too slow to be observed in the Flowing Afterglow, we carried out the investigations described in this paper to elucidate: (i) the pathway by which $O^{-\bullet}$ reacts with trimethylphosphine ultimately to yield $Me_2PCH_2^-$; (ii) the implications of that pathway with regard to the acidity of trimethylphosphine and; (iii) the general reactivity of trimethylphosphine with anions.

Results

In the following sections, we present the results found for a series of room-temperature investigations in which anionic bases (A^-) were allowed to react with trimethylphosphine. For many of these systems, we also examined the reaction of the conjugate base of trimethylphosphine with the parent molecule (AH) of the anionic base in an independent experiment. The results of the reactions detailed below are partially summarized in the Table which contains only the proton-transfer aspects of the reactions. Unless otherwise indicated, all gas-phase acidity values cited in this work are from the standard compilations.[12] For those cases, where we report 'no reaction' it is more proper to say that neither product ions from any reaction nor a decrease in the reactant ion signal were observed within the time window of our instrument. Normally, we estimate that we can measure rate coefficients which are greater than or equal to 1×10^{-13} cm^3 particle^{-1} s^{-1} (the maximum rate coefficient is that of the collision frequency which for the systems examined here is about 2—3 × 10^{-9} cm^3 particle^{-1} s^{-1}) and that we

Table. Acid–base reactions of trimethylphosphine[a]

$\Delta G^{\circ}_{\mathrm{acid}}(\mathrm{AH})$ (kJ mol^{-1})	$\Delta H^{\circ}_{\mathrm{acid}}(\mathrm{AH})$ (kJ mol^{-1})	AH	Is proton transfer observed for: $\mathrm{A^-} + \mathrm{PMe_3}$?	$\mathrm{Me_2PCH_2^-} + \mathrm{AH}$?
1 657 ± 3	1 689 ± 3	$\mathrm{NH_3}$	Yes	
1 616 ± 8	1 646 ± 8	MeSMe	Yes	No
1 607 ± 8	1 635 ± 10	$\mathrm{H_2C{=}CHMe}$	Yes	No
1 607 ± 2	1 635 ± 1	$\mathrm{H_2O}$[b]	Yes	No[c]
1 586 ± 23	1 614 ± 26	$\mathrm{H_2C{=}C(CH{=}CH_2)Me}$	Yes	No
1 574 ± 1	1 599 ± 1	$\mathrm{HO^{\bullet}}$	Yes	
1 565 ± 8	1 593 ± 5	$\mathrm{H_2C{=}C{=}CH_2}$	No	Yes
1 565 ± 8	1 592 ± 9	MeOH	Yes	Yes
1 564 ± 8	1 593 ± 10	PhMe	No	Yes
1 551 ± 8	1 579 ± 10	EtOH	No	Yes

[a] Note that only the acid–base components of an ion–molecule reaction are compiled in this table; see the text for a full description of all channels observed for each ion-neutral pair. Blank entries indicate a reaction that was not examined. Acidities are those taken from the sources cited in the text (see Results section). [b] Acidity values for deuterium oxide are $\Delta G^{\circ}_{\mathrm{acid}}(\mathrm{D_2O})$ 1 619 ± 1 kJ mol^{-1} and $\Delta H^{\circ}_{\mathrm{acid}}(\mathrm{D_2O})$ 1 644 ± 1 kJ mol^{-1}. [c] See text for a full evaluation of the observations for this reaction.

can qualitatively observe some products from reactions that proceed with rate coefficients greater than 1×10^{-14} cm^3 particle^{-1} s^{-1}.

Direct ionization of trimethylphosphine. If trimethylphosphine was directly added across the flow tube from the simple ion source, high yields of ions at *m/z* 75 ($\mathrm{Me_2PCH_2^-}$) and *m/z* 61 ($\mathrm{Me_2P^-}$) are obtained, presumably by the Penning ionization reaction *via* metastable helium atoms.

Ammonia ($\Delta G^{\circ}_{\mathrm{acid}}$ 1 657 ± 3 kJ mol^{-1}; $\Delta H^{\circ}_{\mathrm{acid}}$ 1 689 ± 3 kJ mol^{-1}). Amide ion was observed to react rapidly and quantitatively with trimethylphosphine by proton transfer.

Dimethyl sulphide ($\Delta G^{\circ}_{\mathrm{acid}}$ 1 616 ± 8 kJ mol^{-1}; $\Delta H^{\circ}_{\mathrm{acid}}$ 1 646 ± 8 kJ mol^{-1}). When the conjugate base of dimethyl sulphide is allowed to react with trimethylphosphine, the predominant[5,6] reaction observed is proton transfer [equation (1)]. A small amount of an ion at *m/z* 121 is also found and which is attributed to addition of $\mathrm{MeSCH_2^-}$ to $\mathrm{PMe_3}$ followed by loss of methane from the resulting adduct [equation (2)]. Because both the conjugate base of dimethyl sulphide ($\mathrm{MeSCH_2^-}$) and that of dimethyl phosphine ($\mathrm{Me_2P^-}$) have nominal mass 61, we are unable completely to elucidate the importance of S_N2 displacement on carbon. However, nucleophilic substitution [equation (3)], while apparently present, appears to be the minor component of the overall reaction.

$$\underset{m/z\ 61}{\mathrm{MeSCH_2^-}} + \mathrm{Me_3P} \begin{cases} \longrightarrow \underset{m/z\ 75}{\mathrm{Me_2PCH_2^-}} + \mathrm{MeSMe} & (1) \\ \longrightarrow \underset{m/z\ 121}{\mathrm{Me_2P\bar{C}HSMe}} + \mathrm{CH_4} & (2) \\ \longrightarrow \underset{m/z\ 61}{\mathrm{Me_2P^-}} + \mathrm{MeSCH_2Me} & (3) \end{cases}$$

When the conjugate base of trimethylphosphine was allowed to react with dimethyl sulphide, no reaction was observed.

Propene ($\Delta G^{\circ}_{\mathrm{acid}}$ 1 607 ± 8 kJ mol^{-1}; $\Delta H^{\circ}_{\mathrm{acid}}$ 1 635 ± 10 kJ mol^{-1}). When prop-2-enide is allowed to react with trimethylphosphine, only slow reaction is observed, with both proton transfer and displacement channels important [equations (4) and (6)]. Further, a trace amount of the addition–methane loss pathway is also detected [equation (5)].

$$\mathrm{CH_2{=}CHCH_2^-} + \mathrm{Me_3P} \begin{cases} \longrightarrow \mathrm{Me_2PCH_2^-} + \mathrm{H_2C{=}CHMe} & (4) \\ \longrightarrow \mathrm{Me_2P\bar{C}HCH{=}CH_2} + \mathrm{CH_4} & (5) \\ \longrightarrow \mathrm{Me_2P^-} + \mathrm{H_2C{=}CHCH_2Me} & (6) \end{cases}$$

As was the case for dimethyl sulphide, no reaction was observed between propene and the conjugate base of trimethylphosphine examined in an independent experiment.

Water ($\Delta G^{\circ}_{\mathrm{acid}}$ 1 607 ± 2 kJ mol^{-1}; $\Delta H^{\circ}_{\mathrm{acid}}$ 1 635 ± 2 kJ mol^{-1}). In a clean, fast process [k_7 *ca.* 9×10^{-10} cm^3 particle^{-1} s^{-1}; ADO (average dipole orientation)[13] reaction efficiency 0.4], hydroxide ion (generated from $\mathrm{N_2O}$ and $\mathrm{CH_4}$ or $\mathrm{N_2O}$ and $\mathrm{NH_3}$) reacts exclusively with trimethylphosphine by proton transfer. The rapid-proton-transfer product evidently overwhelms the addition–methane loss route as no product from this latter channel ($\mathrm{Me_2PO^-}$) is detected.

$$\mathrm{HO^-} + \mathrm{PMe_3} \xrightarrow{k_7} \mathrm{Me_2PCH_2^-} + \mathrm{H_2O} \qquad (7)$$

Under the conditions for which this reaction was examined, an ion at *m/z* 101 is observed in fairly high yield. Ingeemann and Nibbering[6] also found this ion. The *m/z* 101 ion is attributed to the conjugate base of trimethylphosphine reacting with nitrous oxide (present by virtue of its role as one of the source gases for $\mathrm{HO^-}$ production) by the well established diazotization[14] reaction of a primary carbanion [equation (8)].

$$\mathrm{Me_2PCH_2^-} + \mathrm{N_2O} \longrightarrow \underset{m/z\ 101}{\mathrm{Me_2PCN_2^-}} + \mathrm{H_2O} \qquad (8)$$

When the conjugate base of trimethylphosphine (prepared by Penning ionization of trimethylphosphine or by proton transfer instigated by $\mathrm{H_2N^-}$) is allowed to react with $\mathrm{D_2O}$, extremely facile and rapid H–D exchange is observed. In this exchange reaction, it is easy to observe all eight protons exchange H for D. In the flowing afterglow mass spectrum, the peaks due to $\mathrm{Me_2PCH_2^-}$ and partially-to-fully deuteriated derivatives account for almost all the ions present. At higher flows of $\mathrm{D_2O}$ at fixed reaction time, *small but equal* amounts of $\mathrm{DO^-}$ and $\mathrm{DO^-(D_2O)}$ are observed. The same behaviour is found for $\mathrm{HO^-}$ and $\mathrm{HO^-(H_2O)}$ in the $\mathrm{Me_2PCH_2^-} + \mathrm{H_2O}$ system. We have been unable to rid either spectrum entirely of these latter two ions. However, based on their intensity behaviour as a function of various experimental parameters, their relative intensities and the remainder of the results reported in this work, we believe that these ions can not be traced to a proton-transfer reaction occurring between $Me_2PCH_2^-$ and D_2O but are rather the result of solvent switching reactions and cluster ion fragmentations.

Isoprene (ΔG°_{acid} 1 586 ± 23 kJ mol^{-1}; ΔH°_{acid} 1 614 ± 26 kJ mol^{-1}). Very slow proton transfer is observed between the conjugate base of isoprene and trimethylphosphine [equation (9)]. The nucleophilic substitution channel was not evident, but some of the reaction does proceed by the addition–methane loss route [equation (10)]. No reaction was observed between the conjugate base of trimethylphosphine and isoprene.

$$H_2C{=}C(CH{=}CH_2)CH_2^- + PMe_3 \longrightarrow \begin{cases} Me_2PCH_2^- + H_2C{=}C(CH{=}CH_2)Me & (9) \\ Me_2P\bar{C}HC(CH{=}CH_2){=}CH_2 + CH_4 & (10) \end{cases}$$

Hydroxyl radical (ΔG°_{acid} 1 574 ± 1 kJ mol^{-1}; ΔH°_{acid} 1 599 ± 1 kJ mol^{-1}). In a fast process (k_{TOT} *ca.* 2×10^{-9} cm^3 particle^{-1} s^{-1}; ADO reaction efficiency 0.7), the atomic oxygen anion reacts with trimethylphosphine predominantly by proton transfer. The other productions observed are those from H-atom transfer, H_2^+ transfer, and addition with loss of a methyl radical.

$$O^{-\bullet} + Me_3P \xrightarrow{k_{101}} \begin{cases} 55\%\ Me_2PCH_2^- + HO\cdot & (11) \\ 25\%\ HO^- + Me_2PCH_2\cdot & (12) \\ 10\%\ C_3H_7P^{-\bullet} + H_2O & (13) \\ 10\%\ Me_2PO^- + Me^\bullet & (14) \end{cases}$$

The branching ratio data reported in equations (11)—(14) is that obtained as described in the Experimental section. In addition, the raw data for each repetition of this branching ratio measurement were corrected for the presence of small amounts of HO^- in the reactant ion spectrum and which reacts with trimethylphosphine as described by equation (7).

While we have not yet optimized our flowing afterglow for accurate absolute rate coefficient measurements, we are able to obtain better estimates of relative rates. Thus we find that $O^{-\bullet}$ reacts with trimethylphosphine 1.8 times more efficiently than does HO^- and that both reactions are very rapid, reaction efficiencies of 40—70%. Three factors serve to reduce the normal accuracy of our branching ratio measurement for the reaction of $O^{-\bullet}$ with PMe_3: (i) HO^- is a significant product of the reaction of $O^{-\bullet}$ with PMe_3, (ii) HO^- reacts rapidly with PMe_3 (*vide supra*), and (iii) typically when we generate $O^{-\bullet}$ we have about a 10% HO^- contamination. Even with these additional limitations on the accuracy of the data for this reaction, it is clear that proton transfer is the major reaction pathway. We have not yet been able to examine the reaction of the conjugate base of trimethylphosphine with hydroxyl radical as the neutral species.

Allene (ΔG°_{acid} 1 565 ± 8 kJ mol^{-1}; ΔH°_{acid} 1 593 ± 5 kJ mol^{-1}).[15] The conjugate base of allene reacts slowly with trimethylphosphine, not by proton transfer, but exclusively by the addition–methane loss pathway [equation (15)].

$$H_2C{=}C{=}CH^- + PMe_3 \longrightarrow Me_2P\bar{C}HC{\equiv}CH + CH_4 \quad (15)$$

The conjugate base of trimethylphosphine reacts at a moderate rate with allene to exclusively yield propadienide from proton transfer.

$$Me_2PCH_2^- + H_2C{=}C{=}CH_2 \longrightarrow C_3H_3^- + PMe_3 \quad (16)$$

Methanol (ΔG°_{acid} 1 565 ± 8 kJ mol^{-1}; ΔH°_{acid} 1 592 ± 9 kJ mol^{-1}).[16] The conjugate base of trimethylphosphine reacts rapidly and exclusively with methanol by proton transfer. When methan[^{2}H]ol is used, exclusive direct D^+ transfer is observed—there is no deuterium incorporation in the unchanged conjugate base of trimethylphosphine. This latter observation implies that once methanol and the conjugate base of trimethylphosphine collide, the only proton-transfer process observable is that to form methoxide ion. On the other hand, methoxide reacts only slowly (k_{TOT} *ca.* 8×10^{-11} cm^3 particle^{-1} s^{-1}) with trimethylphosphine to give products from addition–methane loss, from addition followed by stabilization and from *proton transfer* [equations (17)—(19)]. The branching ratio reported in equations, (17)—(19) is that averaged over three independent measurements at a flow-tube pressure of 40 Pa of helium. Because the addition–stabilization channel is presumably termolecular and not saturated, it is expected that channel (19) will be favoured relative to the others as the flow tube pressure is increased.

$$MeO^- + Me_3P \xrightarrow{k_0} \begin{cases} 16\%\ Me_2PCH_2^- + MeOH & (17) \\ 10\%\ Me(MeO)PCH_2^- + CH_4 & (18) \\ \xrightarrow[{[He]}]{} 74\%\ Adduct^- & (19) \end{cases}$$

Toluene (ΔG°_{acid} 1 564 ± 8 kJ mol^{-1}; ΔH°_{acid} 1 593 ± 10 kJ mol^{-1}). $Me_2PCH_2^-$ reacts with toluene in a slow reaction by exclusive proton transfer [equation (20)]. Toluenide reacts slowly with trimethylphosphine, but in this latter case the sole product is that from the addition–methane loss reaction [equation (21)].

$$Me_2PCH_2^- + PhMe \longrightarrow PhCH_2^- + PMe_3 \quad (20)$$

$$PhCH_2^- + PMe_3 \longrightarrow Me_2P\bar{C}HPh + CH_4 \quad (21)$$

Ethanol (ΔG°_{acid} 1 551 ± 8 kJ mol^{-1}; ΔH°_{acid} 1 579 ± 10 kJ mol^{-1}).[16] $Me_2PCH_2^-$ reacts rapidly with ethanol by proton transfer [equation (22)] while ethoxide reacts with trimethylphosphine by competitive addition–stabilization and addition–methane loss [equations (23)—(25)].

$$Me_2PCH_2^- + EtOH \longrightarrow EtO^- + PMe_3 \quad (22)$$

$$EtO^- + PMe_3 \longrightarrow \begin{cases} Me(EtO)PCH_2^- + CH_4 & (23) \\ Me_2PO^- + CH_4 + H_2C{=}CH_2 & (24) \\ Adduct^- & (25) \end{cases}$$

Discussion

Gas-phase Acidity of Trimethylphosphine.—The first important conclusion of the set of results reported above concerns the gas-phase acidity of trimethylphosphine. We find that trimethylphosphine reacts exclusively with H_2N^- by proton transfer. Furthermore, both $MeSCH_2^-$ and $H_2C{=}CHCH_2^-$ are observed to react with trimethylphosphine to a significant extent by proton abstraction. The $Me_2PCH_2^-$ ion does not react with dimethyl sulphide or propene. Thus, one can conclude that trimethylphosphine is more acidic than propene. Ingemann and Nibbering[6] reported identical results for the ammonia and dimethyl sulphide systems (though they did not examine the propene system).

We found that HO^- reacts rapidly and exclusively with trimethylphosphine by proton abstraction. When the conjugate base of trimethylphosphine is allowed to react with water, only very slow formation of HO^- is observed and the rate of HO^- production is identical to that of $HO^-(H_2O)$ production. When the conjugate base of trimethylphosphine is allowed to react with D_2O, the same type of behaviour is observed for DO^- and $DO^-(D_2O)$ but in addition, extremely fast H/D exchange is observed. Thus the experimental data for the water system indicate that trimethylphosphine is more acidic than water. The question remains as to how much more acidic trimethylphosphine is than water.

At the other end of the range of acids examined, we find that $Me_2PCH_2^-$ abstracts a proton both from allene (moderate rate), methanol (fast), toluene (slow), and ethanol (fast) while neither ethoxide, toluenide, nor propadienide appear to abstract a proton from trimethylphosphine. From this latter set of reactions, we conclude that trimethylphosphine is less acidic than allene. Thus the acidity of trimethylphosphine is bracketed between water (ΔG°_{acid} 1 607 kJ mol^{-1}) and allene (ΔG°_{acid} 1 565 kJ mol^{-1}). In order to tighten the limiting bracket values on the acidity of trimethylphosphine even further, we examined the hydroxyl radical and methanol systems in considerable detail.

Consider first the methanol system. As reported above, only 16% of the methoxide–trimethylphosphine reaction yields $Me_2PCH_2^-$ while the majority of the reaction proceeds by way of (presumably) termolecular adduct or cluster formation. The small yield of proton transfer as compared with the higher yield of adduct is an indication that methanol is more acidic than trimethylphosphine [*i.e.*, $\Delta G^\circ_{acid}(PMe_3) > 1\,565$ kJ mol^{-1}], but not drastically so. Indeed, using (i) our measured rate coefficient for the total reactive decay rate of MeO^- with PMe_3, (ii) our measured yield of the proton-transfer channel, and (iii) assuming that $Me_2PCH_2^-$ abstracts a proton from methanol at the collision rate (certainly justified by our qualitative experiments), then we calculate trimethylphosphine to be about 13 kJ mol^{-1} less acidic than methanol or $\Delta G^\circ_{acid}(PMe_3) \sim 1\,577$ kJ mol^{-1}.

Confirmation of the methanol-derived conclusion comes from the hydroxy system. Here, we were able to examine only the reaction of the atomic oxygen anion with trimethylphosphine; we are not able to use the hydroxyl radical as the neutral species in an ion-molecule reaction. As reported above, we find in this case that the reaction is also efficient and it gives predominantly proton-transfer product. These results clearly indicate that the acidity of trimethylphosphine must be very similar to that of the hydroxyl radical. Using (i) our measured rate coefficient for the total reactive decay of $O^{-\bullet}$ with PMe_3, (ii) our measured yield of the proton-transfer channel, and (iii) assuming that $Me_2PCH_2^-$ abstracts a proton from hydroxyl radical at the collision frequency (currently an unverified assumption) then we calculate trimethylphosphine to be *ca.* 3 kJ mol^{-1} less acidic than the hydroxyl radical or $\Delta G^\circ_{acid}(PMe_3) \sim 1\,577$ kJ mol^{-1}.

Taken as a whole, the set of reactions examined in this report demand that the acidity of trimethylphosphine be similar to that of the hydroxyl radical. We therefore recommend $\Delta G^\circ_{acid}(PMe_3)$ 1 577 ± 13 kJ mol^{-1}. Using[6] $\Delta S^\circ_{acid}(PMe_3)$ 102 J K^{-1} mol^{-1} gives $\Delta H^\circ_{acid}(PMe_3)$ 1 607 ± 13 kJ mol^{-1}. The major portion of error associated with the final acidity values reflects uncertainties in the reference acids and, to a much lesser extent, uncertainties in the relative placement of trimethylphosphine with respect to the reference acids. The small HO^- and $HO^-(H_2O)$ signals observed in the water–trimethylphosphine system are disturbing, but they do not behave as primary and secondary product ions. In particular, the first hydrate appears at the same time as does the hydroxide ion which is not consistent with formation of HO^- by proton transfer followed by termolecular stabilization to give the hydrate.[17]

A few control experiments were run to ensure that we correctly evaluated the data on hand. One of the cornerstones of the revised estimate for the acidity of trimethylphosphine is the data from the methoxide studies in which we found that 16% of the reaction proceeds by proton transfer. This latter observation is incompatible with[6] $\Delta G^\circ_{acid}(PMe_3)$ 1 606 ± 8 kJ mol^{-1}. When we examined the reaction of methoxide with propene, an acid whose acidity is very close to the previously reported trimethylphosphine acidity [$\Delta G^\circ_{acid}(H_2C{=}CHMe)$ 1 607 ± 8 kJ mol^{-1}], under identical conditions to those employed for the trimethylphosphine experiments, no trace of proton transfer is observed! These control experiments provide further confirmation that energetic ions are not contributing to the reactions detected in the flowing afterglow investigations of this reaction.

Another critical observation on which the new acidity value of trimethylphosphine is based is the reaction of the atomic oxygen anion to yield 55% proton-transfer products. This product yield is that corrected to eliminate any contributions from secondary reactions in the normal fashion.[18] However, to ensure that we could indeed discriminate between $Me_2PCH_2^-$ formed from primary [equation (26)] *versus* secondary reactions [equation (27)] we examined the reaction of $O^{-\bullet}$ with

$$O^{-\bullet} + PMe_3 \longrightarrow Me_2PCH_2^- + HO^{\bullet} \qquad (26)$$

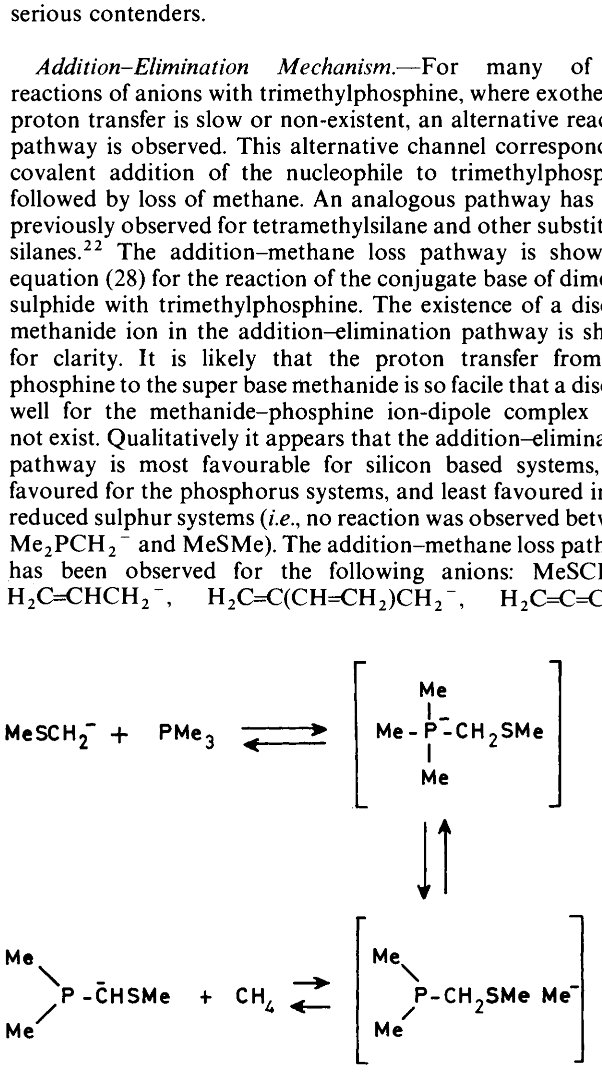
$$\begin{array}{l} O^{-\bullet} + PMe_3 \longrightarrow HO^- + Me_2PCH_2^{\bullet} \\ \qquad\qquad\qquad\quad \big\lfloor \xrightarrow{PMe_3} Me_2PCH_2^- + H_2O \end{array} \qquad (27)$$

propene, for which the direct proton transfer in endoergic by 33 kJ mol^{-1}. For the reaction of $O^{-\bullet}$ wiith propene in the flowing afterglow prop-2-enide can be observed in relatively high yield. For this latter reaction we found that quite demonstrably our data analysis was able to show that HO^- is the principal primary product (90% yield, 10% yield of the $M - H_2^{+}$ anion) and that it reacts rapidly in a secondary process to give prop-2-enide [akin to equation (27)]. When we compare the behaviour of $O^{-\bullet}$ with propene to that of trimethylphosphine, we found them to be quite different and that HO^- is not the principal primary product ion for trimethylphosphine.

As was mentioned in the Results section, we also examined the trimethylphosphine–isoprene system in both directions. In accord with the acidity value derived above for trimethylphosphine, we find that the conjugate base of trimethylphosphine does not abstract a proton from isoprene but that the conjugate base of isoprene does abstract a proton from trimethylphosphine. However, these data for the isoprene system only indirectly support our acidity value since the gas-phase acidity of isoprene is not well known [ΔG°_{acid}(isoprene) 1 586 ± 23 kJ mol^{-1}] and because the observed direction of proton transfer is very slow. Recent measurements from our laboratory indicate that the gas-phase acidity of isoprene is probably closer to that of the hydroxyl radical than to water, as the atomic oxygen anion, when allowed to react with isoprene, yields about 40% proton-transfer products.[19]

The competitive bimolecular and (presumably) termolecular reactions observed when either methoxide or ethoxide are allowed to react with trimethylphosphine are noteworthy. Normally, observed bimolecular processes will overwhelmingly dominate any termolecular reaction channels. However, Ferguson, Smith, and Adams[20] have shown how termolecular associations can have enhanced rate coefficients by the presence of an endothermic bimolecular channel which 'traps' the collision complex. The relatively long-lived complex results from conversion of translational energy necessary for ion–neutral species return to separated reactants into chemical energy used to fuel the endothermic process. The enhanced lifetime is manifested by a large rate coefficient for three-body association—or in our case, by successful competition between bimolecular and termolecular channels. Even though the bimolecular channel is formally endothermic (as in the case of proton transfer from trimethylphosphine to the alkoxide), the occurrence within the ion–molecule complex can give rise to a new ion–molecule complex with more favourable electrostatic interactions (*i.e.*, compare solvation energies of [$MeO\cdot^{-}PMe_3$] and [$MeOH^{-}\cdot CH_2PMe_2$]).[21] At this point, the exact structure of the adducts remains unknown; however, the behaviour discussed above suggests that either a covalent adduct or an alcohol conjugate base of trimethylphosphine complex are serious contenders.

Addition–Elimination Mechanism.—For many of the reactions of anions with trimethylphosphine, where exothermic proton transfer is slow or non-existent, an alternative reaction pathway is observed. This alternative channel corresponds to covalent addition of the nucleophile to trimethylphosphine followed by loss of methane. An analogous pathway has been previously observed for tetramethylsilane and other substituted silanes.[22] The addition–methane loss pathway is shown in equation (28) for the reaction of the conjugate base of dimethyl sulphide with trimethylphosphine. The existence of a discrete methanide ion in the addition–elimination pathway is shown for clarity. It is likely that the proton transfer from the phosphine to the super base methanide is so facile that a discrete well for the methanide–phosphine ion-dipole complex does not exist. Qualitatively it appears that the addition–elimination pathway is most favourable for silicon based systems, less favoured for the phosphorus systems, and least favoured in the reduced sulphur systems (*i.e.*, no reaction was observed between $Me_2PCH_2^-$ and MeSMe). The addition–methane loss pathway has been observed for the following anions: $MeSCH_2^-$, $H_2C{=}CHCH_2^-$, $H_2C{=}C(CH{=}CH_2)CH_2^-$, $H_2C{=}C{=}CH^-$, MeO^-, and $PhCH_2^-$. The only cases where the adduct or cluster ion has been observed at 40 Pa total pressure are in the water, methanol, and ethanol systems. Thus it appears as if the lifetime of the tetravalent phosphide anion is too short to be collisionally stabilized to any appreciable degree. In fact, the addition–methane loss pathway itself is a rather slow one in that it is observed only when other more facile pathways are prevented from occurring. For example, by making proton transfer endothermic, fast proton transfer is precluded, then one sees the addition–methane loss channel.



(28)

Conclusions

By using the bracketing technique on a Flowing Afterglow, we have shown that the gas-phase acidity of trimethylphosphine is similar to that of the hydroxyl radical. Our findings are in slight contrast to previous ICR measurements[6] and recent theoretical calculations.[9] We recommend the following values: $\Delta G^{\circ}_{acid}(PMe_3)$ 1 577 ± 13 kJ mol^{-1}, $\Delta H^{\circ}_{acid}(PMe_3)$ 1 607 ± 13 kJ mol^{-1}. In addition to proton transfer, we have discovered a new pathway for the interactions of gaseous anions with trimethylphosphine, namely addition of the anion to the phosphine to give (presumably) the covalent adduct anion, which then decomposes by loss of methane. Further investigations into the gas-phase chemistry of alkylphosphines and this intriguing addition–elimination process are in progress. Work is also in progress to investigate the gas-phase chemistry of the dimethyl phosphinide anion generated from Penning ionization of trimethylphosphine.

Experimental

These experiments were carried out at ambient temperature (298 ± 3 K) utilizing a recently constructed flowing afterglow which has been described previously.[11] The total pressure in the reaction region (flow tube) was typically 40 Pa, and was established by maintaining a constant volumetric flow rate of helium [7.18 l min^{-1} (s.t.p.)]. The primary reactant ions, H_2N^-, $O^{-\bullet}$, and MeO^-, were generated by dissociative electron attachment to ammonia (partial pressure 0.4 Pa), nitrous oxide, or methyl nitrite[23] (partial pressure of less than 0.1 Pa) directly in the upstream portion of the reaction region. When generating $O^{-\bullet}$ we typically observed a contaminant HO^- signal that was 10% or less as intense as the $O^{-\bullet}$ signal. The contaminant hydroxide is probably due to H-atom abstraction by $O^{-\bullet}$ from adventitious hydrocarbons such as methane. For certain experiments, HO^- was cleanly generated by allowing the atomic oxygen anion (generated from a partial pressure of 0.3 Pa of nitrous oxide) to abstract an H atom from high-purity methane or ammonia (partial pressure 0.3 Pa). Other reactant ions were formed by exothermic proton transfer from the appropriate neutral to one of the primary ions [*e.g.*, $CH_2{=}CHCH_2^-$ from H_2N^- and $CH_2{=}CHMe$ or $Me_2PCH_2^-$ from H_2N^- and PMe_3]. In addition to electron impact ionization of methyl nitrite,[23] MeO^- was formed by reaction of amide ion with either methanol or dimethoxyethane.[24] When switching between H_2N^- and $O^{-\bullet}$ as reactant ions, both with nominal mass-to-charge ratio of 16, we confirmed the ion identity by its reaction with benzene. Amide ion is known rapidly and exclusively to abstract a proton from benzene while $O^{-\bullet}$ gives several products,[25] most notably $C_6H_4^{-\bullet}$. We found this simple check to be useful as on several occasions supposed amide ion production from ammonia turned out to be $O^{-\bullet}$. The situations where confusion arose were those where only a trace of ammonia (too small to affect noticeably the overall flow tube pressure, *i.e.*, partial pressure < 0.01 Pa) was being added. When generating amide from the more common conditions (partial pressure of ammonia in the flow tube of 0.3 Pa), we found the m/z 16 ion to be only H_2N^-.

Neutral reagents were added to the instrument by means of a dedicated glass vacuum system. Liquid samples were handled in round-bottom flasks fitted with high-vacuum stopcocks; each sample was subjected to several freeze-pump-thaw cycles to remove dissolved gases. Volumetric flow rates of neutrals were determined by measuring pressure rise in a calibrated volume.[11] The branching ratios reported are those corrected to eliminate any contributions from secondary reactions[18] and are obtained by measuring relative ion concentrations as a function of concentration of the neutral reagents at fixed reaction time. The course of all reactions was examined qualitatively, under pseudo-first-order conditions at fixed reaction time by taking a complete mass spectrum at each of several different concentrations of the neutral reagent. When necessary, the branching ratio data were also corrected to remove contributions from parallel reactions that gave the same ion products [*i.e.*, for the $O^{-\bullet}$ + PMe_3 reaction, correction was made for equation (7) due to the contaminant HO^- in the 'trimethylphosphine-free' reactant ion spectrum].

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