Unusual Reactivity of the Radical Cations of Some Simple Trivalent Organophosphorus Compounds toward Dimethyl Disulfide and Dimethyl Diselenide

Rebecca L. Smith,[†] Andreas Schweighofer,[‡] Helmut Keck,[‡] Wilhelm Kuchen,[‡] and Hilkka I. Kenttämaa*,[†]

Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907-1393, and Department of Inorganic and Structural
Chemistry I, Heinrich Heine University, Düsseldorf, Düsseldorf, Germany

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Abstract: Dimethyl disulfide and dimethyl diselenide are known to readily undergo charge exchange with gaseous conventional radical cations containing oxygen, nitrogen, and sulfur functionalities. In sharp contrast, the radical cations of trimethylphosphine and trimethyl phosphite rapidly abstract $CH_3S^\bullet$ and $CH_3Se^\bullet$ groups from dimethyl disulfide and dimethyl diselenide, respectively, in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer. These sorts of abstraction reactions have been reported earlier only for distonic radical cations (ions with spatially separated charge and radical sites). Isomerization of the organophosphorus radical cations to their distonic forms *prior to* or during the reaction was ruled out by demonstrating that the connectivity in $(CH_3)_3P^{\bullet+}$ does not change during the reaction: the $CH_3S^\bullet$ abstraction product has the structure $(CH_3)_3P^+{-}SCH_3$. Instead, the abstraction reactions are likely initiated by thermoneutral charge exchange. The neutral phosphorus compound then replaces a $CH_3S^\bullet$ or $CH_3Se^\bullet$ group in ionized dimethyl disulfide and ionized dimethyl diselenide, respectively. In support of this mechanism, three different neutral phosphorus compounds were shown to replace $CH_3S^\bullet$ in the radical cation of dimethyl disulfide. Phosphorus radical cations with high recombination energies were found to react with dimethyl disulfide by exclusive charge exchange. Hence, the abstraction reactions require a radical cation with a recombination energy close to the ionization energy of dimethyl disulfide (8.1 eV) and dimethyl diselenide (7.9 eV). Further, the reactions seem to be limited to phosphorus-containing ions since radical cations with nitrogen and sulfur functionalities do not undergo these reactions even when their recombination energies are close to 8.1 eV.

Introduction

Dimethyl disulfide provides[1] a useful chemical tool for the differentiation of gaseous distonic radical cations (ions with spatially separated charge and radical sites[2]) from their conventional isomers. Distonic ions commonly abstract a $CH_3S^\bullet$ group from this molecule while conventional radical cations either react by charge exchange or are unreactive.[1] This difference in reactivity has been utilized in the structural characterization of various organic radical cations, including the conventional and distonic forms of ionized trimethylene oxide[1] and ethyl methyl sulfide.[3] Dimethyl diselenide[4] was recently reported to react with radical cations analogously to dimethyl disulfide; abstraction of $CH_3Se^\bullet$ is typically observed for distonic ions while conventional radical cations react with dimethyl diselenide by charge exchange.[4]

The general reactivity characteristics described above apply to radical cations containing oxygen, nitrogen, and sulfur functionalities.[1,3,4] We report here the first investigation of the reactions of simple *conventional organophosphorus* radical cations with dimethyl disulfide and dimethyl diselenide. In sharp contrast to all other conventional radical cations studied thus far, the radical cations of trimethylphosphine and trimethyl phosphite (but not methylphosphine) were found to react with dimethyl disulfide and dimethyl diselenide by rapid $CH_3S^\bullet$ and $CH_3Se^\bullet$ abstraction, respectively. The generality and mechanism of these reactions are discussed.

Experimental Section

All experiments were performed using an Extrel Model 2001 Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR). This instrument contains a dual cell consisting of two identical cubic 2-in. cells, joined by a common wall (the conductance limit). The cell is aligned within the magnetic field produced by a 3.0 T superconducting magnet. The dual cell is differentially pumped to a base pressure of $<10^{-9}$ Torr (in the cell) by using two Balzers turbomolecular pumps (330 L/s), each backed by an Alcatel 2012 mechanical pump.

Samples were introduced into the instrument by using two Extrel-manufactured single batch inlet systems equipped with variable leak valves, a Varian leak valve, a pulsed valve setup,[5a] or a solids probe. The nominal reagent pressures in the cell ranged from 4.0×10^{-8} up to 1.4×10^{-7} Torr, as measured with two ionization gauges located on both sides of the dual cell. Ions were generated from a sample introduced into the cell by passing an electron beam through the center of the dual cell. The ion signal was optimized for each experiment by varying the electron energy (typically 20 to 50 eV), the emission current (either 4 or 8 μA), and the ionization time (typically 30 to 50 ms). In

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[†] Purdue University.

[‡] Heinrich Heine University.

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(1) Stirk, K. M.; Orlowski, J. C.; Leeck, D. T.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8604.

(2) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225.

(3) Smith, R. L.; Chyall, L. J.; Stirk, K. M.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1993**, *28*, 1623.

(4) Beasley, B. J.; Smith, R. L.; Kenttämaa, H. I. *J. Mass Spectrom.* **1995**, *30*, 384.

(5) (a) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571. (b) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (c) Grosshans, P. B.; Marshall, A. G. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 347.

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Table 1. Reactions of Organophosphorus Radical Cations with the Neutral Reagents Studied

	dimethyl disulfide (%)		dimethyl diselenide (%)		triethylamine (%)	
reactant ion	eff.[a]	reaction	eff.[a]	reaction	eff.[a]	reaction
$CH_3PH_2^{\bullet+}$	1.0	charge exchange (100)	1.0	charge exchange (100)	1.0	charge exchange (90) proton transfer (10)
$(CH_3)_3P^{\bullet+}$	0.51	$^\bullet SCH_3$ abstraction (100)	0.50	$^\bullet SeCH_3$-abstraction (100)	0.64	charge exchange (100)
$(CH_3O)_3P^{\bullet+}$	0.50	$^\bullet SCH_3$ abstraction (≃90) charge exchange (≃10)	low	$^\bullet SeCH_3$-abstraction (100)	0.69	charge exchange (100)

[a] eff = k_{exp}/k_{coll}.

some cases, the primary ions were allowed to react with neutral reagents added into the same cell in order to form the desired ions by ion−molecule reactions.

Ions formed by the electron beam were transferred from the cell in which they were generated into the other cell by grounding the conductance plate (typically for 100 μs) which allowed the ions to pass through the 2-mm hole in this plate. Before ion transfer, ions generated in the other cell by the electron beam were removed by applying a negative potential (−10 V) to the remote trapping plate of that cell (typically for 5 ms). At all other times, this plate and the other two trapping plates perpendicular to the magnetic field were kept at +2 V. The transferred ions were kinetically and internally cooled through collisions (50−100) with argon introduced into the cell via a set of pulsed valves (peak pressure 1×10^{-5} Torr in the cell). After collisional cooling, all the interfering ions were removed from the cell by using the stored-waveform inverse Fourier-transform method[6] (Extrel SWIFT module). Care was taken to avoid kinetic excitation of the ions to be studied.

The isolated ions were allowed to react with a neutral reagent for a variable period of time. The reactions follow pseudo-first-order kinetics. Thus, the experimental rate constant of each ion−molecule reaction (k_{exp}) was obtained from a semilogarithmic plot of the relative abundance of the reactant ion *versus* time. The accuracy of the rate constant measurements is estimated to be ±50% while the precision is better than ±10%. The pressure readings were corrected for the sensitivity[7a] of the ion gauge toward each neutral reagent and for the pressure gradient between the dual cell and the ion gauge. The latter correction was obtained by measuring rates of reactions with known rate constants involving each neutral molecule. The collision rate constant (k_{coll}) was calculated using the parametrized trajectory theory.[7b] The reaction efficiencies are given as k_{exp}/k_{coll}. Branching ratios were determined from the relative abundances of the product ions at short reaction times.

Collision-activated dissociation[5b] (CAD) was used to examine the structure of several of the product ions. The ions were generated by ion−molecule reactions in one cell and transferred into the other cell which contained a nominal pressure of 1×10^{-7} Torr of argon. The ions were cooled by allowing them to collide with argon for 1 s. The ions were isolated and accelerated by using an on-resonance rf pulse (3.5 V_{p-p}). By varying the length of the excitation pulse, the ions were excited to different kinetic energies. The excited ions were dissociated by allowing them to collide with argon for 100 ms (on average, the ions undergo only one collision) and then detected in the usual manner. The reported ion kinetic energies are laboratory kinetic energies corrected as recommended by Grosshans and Marshall,[5c] i.e., by taking half the value computed according to the infinite parallel plate approximation.

All the spectra obtained are an average of at least 20 transients. The ions were excited for detection by the stored-waveform inverse Fourier-transform method with 0.5 cm final radius for all ions. The spectra were recorded as 64k data points at a digitizer rate of 5.3 MHz and were subjected to one zero fill before Fourier transformation.

Methylphosphine was synthesized by a two-step procedure from $CH_3P(S)Cl_2$ as described previously[8a] and used as a CH_3PH_2−HI complex.[8b] The identity and purity of this compound were determined by GC/MS. All other reagents were obtained commercially and checked for purity by mass spectrometry.

Table 2. Ionization Energies (IE) of the Reagents Used in This Work

reagent	IE (eV)	reagent	IE (eV)
methylphosphine	9.12[a]	dimethyl disulfide	8.1[b]
trimethylphosphine	8.06[a]	dimethylc diselenide	7.9[c]
trimethyl phosphite	8.5[a]	triethylamine	7.5[a]

[a] Values from ref 11. [b] Values from ref 13. [c] Values from ref 14.

Results and Discussion

Methylphosphine, trimethylphosphine, and trimethyl phosphite radical cations were generated in one side of the dual cell reaction chamber, transferred into the other side, isolated by ejecting all other ions out of the cell, and allowed to react with dimethyl disulfide and dimethyl diselenide for a variable period of time. The efficiency (ratio of reaction rate to collision rate = k_{exp}/k_{coll}) and the branching ratios of the ionic products were determined for each reaction (Table 1).

As expected, the reactions of the methylphosphine radical cation with dimethyl disulfide and dimethyl diselenide are dominated by charge exchange which is highly exothermic ($\Delta H_{reaction} = -24$ kcal/mol for dimethyl disulfide; $\Delta H_{reaction} = -28$ kcal/mol for dimethyl diselenide; Table 2). In sharp contrast, the radical cations of trimethylphosphine and trimethyl phosphite react with these neutral reagents by predominant $CH_3X^\bullet$ abstraction (X = S, Se). This finding was unexpected for two reasons. First, charge exchange would be thermoneutral or exothermic for both of these radical cations (Table 2) and hence expected to occur readily. Further, this type of an abstraction reaction has been previously reported only for distonic ions.[1,3,4,9]

The unexpected reactivity described above for the trimethylphosphine and trimethyl phosphite radical cations prompted an examination of their structures and of the mechanism through which the $CH_3S^\bullet$ and $CH_3Se^\bullet$ abstraction reactions take place. The results are discussed below, with a focus on the abstraction of $CH_3S^\bullet$ from dimethyl disulfide by $(CH_3)_3P^{\bullet+}$.

Structural Characterization of the Trimethylphosphine Radical Cation. Many long-lived organic radical cations are known to spontaneously isomerize to more stable distonic forms in the gas phase and in the condensed phase.[10] Isomerization of the radical cation of trimethylphosphine to its distonic form $(CH_3)_2PH^+-CH_2^\bullet$ *prior to* or during the reaction with dimethyl disulfide and dimethyl diselenide would readily explain the observation of $^\bullet XCH_3$ abstraction (X = S, Se) from these reagents.

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(6) Wang, T.-C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1986**, *58*, 2938.

(7) (a) Bartmess, J. E.; Georgiadis, R. M. *Vacuum* **1983**, *33*, 149. (b) Su, T.; Chesnavich, W. J. *J. Chem. Phys.* **1982**, *76*, 5183.

(8) (a) Bissey, J. E.; Goldwhite, H.; Rowsell, D. G. *J. Org. Chem.* **1967**, *32*, 1542. (b) Tommes, P. Ph.D. Dissertation, University of Düsseldorf, 1995.

(9) Smith, R. L.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1995**, *117*, 1393.

(10) See, for example: (a) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (b) Stirk, K. M.; Kiminkinen, L. K. M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649. (c) Symons, M. C. R. *Chem. Soc. Rev.* **1984**, 393. (d) Leeck, D. T.; Stirk, K. M.; Zeller, L. C.; Kiminkinen, L. K. M.; Castro, L. M.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1994**, *116*, 3028.

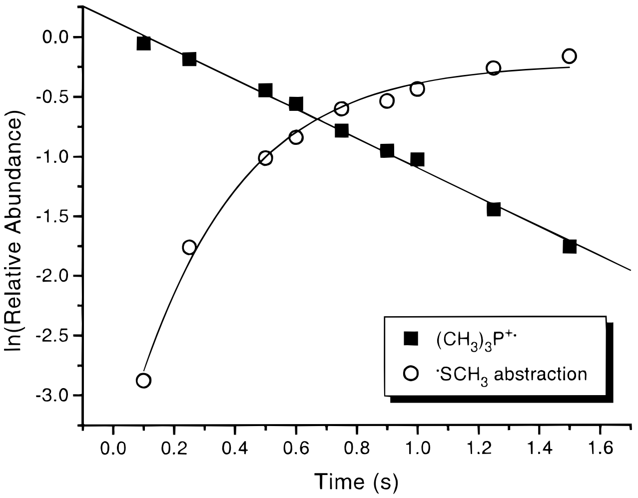

Figure 1. Temporal variation of the relative abundances of the reactant ion and the ionic products generated upon reaction of ionized trimethylphosphine (*m/z* 76) with dimethyl disulfide (MW 94). The nominal pressure of dimethyl disulfide was 1.2 × 10^{-7} Torr.

The ion population formed upon ionization of trimethylphosphine is likely to be composed of ions with only one structure since all the reactions studied follow pseudo-first-order kinetics (Figure 1). The structure of the ions was probed through reaction with triethylamine. This reagent has a very low ionization energy (7.5 eV).[11] Hence, an ion with the conventional structure $(CH_3)_3P^{\bullet+}$ is expected[10d] to react with triethylamine by facile charge exchange ($\Delta H_{rxn} \approx -13$ kcal/mol; Table 2). However, if the ion had rearranged to the distonic ion $(CH_3)_2PH^+{-}CH_2^{\bullet}$, deprotonation should take place since distonic ions of this type are generally[12] stronger acids than the corresponding even-electron ions (ions which would be generated by attaching a hydrogen atom to the radical site of the distonic ion; the proton affinity[11] of $(CH_3)_3P$ is 227.1 kcal/mol, that of triethylamine is 232 kcal/mol). Moreover, neutralization of the ion $(CH_3)_2PH^+{-}CH_2^{\bullet}$ by electron transfer would be highly endothermic.[2a] Exclusive and facile charge exchange was observed upon the reaction of the trimethylphosphine radical cation with triethylamine (Table 1). This finding strongly suggests that the reactant ion possesses the conventional structure $(CH_3)_3P^{\bullet+}$. The same result was obtained for the ions $(CH_3O)_3P^{\bullet+}$ and $CH_3PH_2^{\bullet+}$. Also these ions react with triethylamine by exclusive or predominant charge exchange (Table 1).

In order to further examine the structure of the trimethylphosphine radical cation, the $CH_3S^{\bullet}$ abstraction product of this ion was isolated and subjected to collision-activated dissociation. The ion decomposes by loss of $^{\bullet}CH_3$, CH_3CH_3, $^{\bullet}SCH_3$, and CH_3SH (the elemental compositions of the ions were assigned on the basis of accurate mass measurements) (Figure 2a). The dissociation product distribution obtained is identical to that obtained for the reference ion $(CH_3)_3P^+{-}SCH_3$ (Figure 2b) formed by transfer of CH_3^+ to $(CH_3)_3PS$ from $CH_3OCH_2^+$ (fragment of ionized dimethyl ether). Furthermore, the variation of the relative abundances of the dissociation products as a function of collision energy is similar for these two ions. All these findings strongly suggest that the trimethylphosphine radical cation has the connectivity $(CH_3)_3P^{\bullet+}$ and that it does not rearrange to the distonic ion $(CH_3)_2PH^+{-}CH_2^{\bullet}$ *prior to* or during the $CH_3S^{\bullet}$ abstraction reaction.

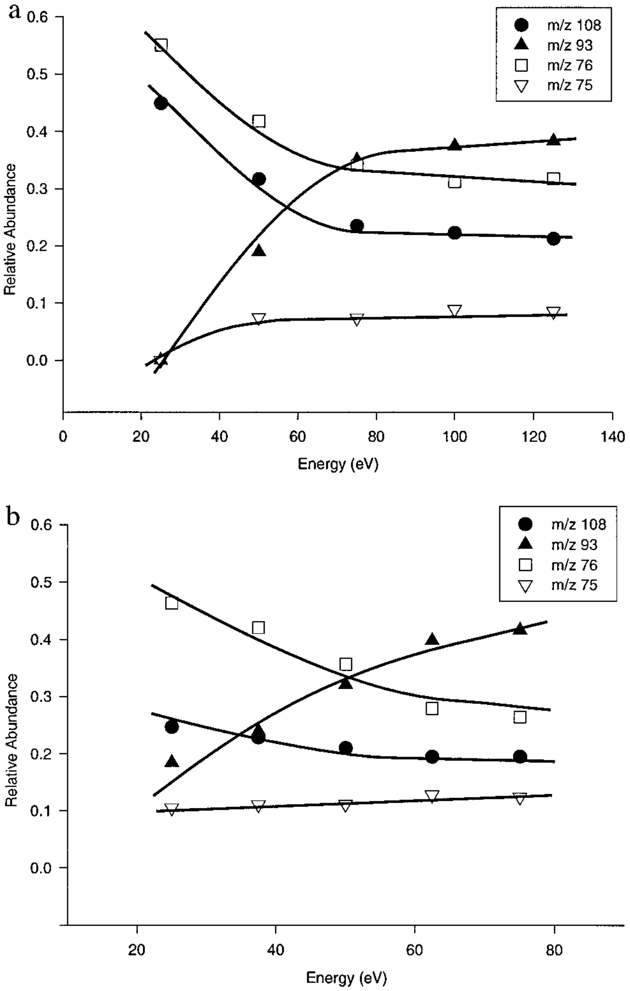

Figure 2. (a) Energy-resolved collision-activated dissociation of the ion (*m/z* 123) formed by $CH_3S^{\bullet}$ abstraction from dimethyl disulfide by ionized trimethylphosphine. (b) Energy-resolved collision-activated dissociation of the reference ion $(CH_3)_3P^+{-}SCH_3$ synthesized by transfer of CH_3^+ from $CH_3OCH_2^+$ to $(CH_3)_3PS$. The collision time for both experiments was 100 ms and the nominal argon pressure was 1.0 × 10^{-7} Torr. The ion of *m/z* 108 corresponds to loss of $CH_3^{\bullet}$, *m/z* 93 to loss of C_2H_6, *m/z* 76 to loss of $^{\bullet}SCH_3$, and *m/z* 75 to loss of $HSCH_3$.

Mechanism of $CH_3X^{\bullet}$ Abstraction (X = S, Se). Due to the low ionization energies of dimethyl disulfide[13] and dimethyl diselenide[14] (8.1 and 7.9 eV, respectively), conventional radical cations generally readily react with these molecules by charge exchange. Those ions that have significantly lower recombination energies ($\ll$8.0 eV) are usually unreactive.[4,13a,14]

The recombination energy of the trimethylphosphine radical cation (8.06 eV; Table 2) is very close to that of dimethyl disulfide and dimethyl diselenide. Hence, although this ion may be neutralized by charge exchange, the reaction is associated with a much smaller driving force than the neutralization of most conventional radical cations studied thus far. The resulting ion−molecule complex (consisting of the dimethyl disulfide radical cation and neutral trimethylphosphine) is of nearly the same energy as the complex of the reactants (neutral dimethyl disulfide and the trimethylphosphine radical cation). This complex is likely to be relatively long-lived. It is conceivable that further reactions take place within this complex. Specifically, it is likely that the neutral trimethylphosphine, a strong

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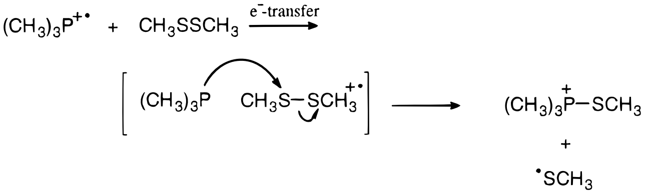
(11) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*.

(12) Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 111.

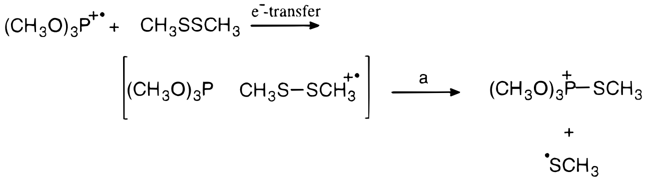
(13) (a) Leeck, D. T.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 106. (b) Li, W.-K.; Chiu, S.-W.; Ma, Z.-X.; Liao, C.-L.; Ng, C. Y. *J. Chem. Phys.* **1993**, *99*, 8440.

(14) Thoen, K. K.; Beasley, B. J.; Smith, R. L.; Kenttämaa, H. I. Submitted for publication.

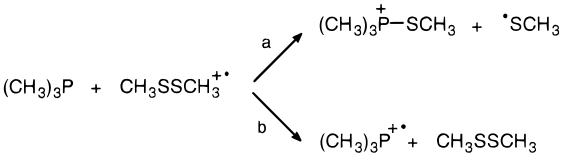
Scheme 1



Scheme 2



Scheme 3



nucleophile, reacts with the dimethyl disulfide radical cation by nucleophilic substitution of $CH_3S^\bullet$ to generate the observed $CH_3S^\bullet$ abstraction product (Scheme 1).

The mechanism proposed above is supported by the finding that the trimethyl phosphite radical cation, another radical cation with a recombination energy close to that of dimethyl disulfide (Table 2), also reacts with dimethyl disulfide by predominant abstraction of $CH_3S^\bullet$ (Scheme 2). In this case, charge exchange has a greater driving force than for the trimethylphosphine radical cation, being exothermic by 9 kcal/mol (Table 2). As a result, a small proportion of the collision complexes formed upon neutralization of the trimethyl phosphite radical cation decomposes without a further reaction. In the case of the methylphosphine radical cation, charge exchange is highly exothermic ($\Delta H_{\mathrm{rxn}} \approx -24$ kcal/mol; Table 2) and dominates the outcome of the reaction with dimethyl disulfide.

The above findings strongly suggest that thermoneutral charge exchange between the radical cation and dimethyl disulfide is a crucial step in the pathway leading to $CH_3S^\bullet$ abstraction by conventional radical cations. Further support for this proposal was obtained from the examination of the reactions involving dimethyl diselenide. Again, the trimethylphosphine and trimethyl phosphite radical cations (with recombination energies close to that of dimethyl diselenide) abstract a $CH_3Se^\bullet$ group while charge exchange dominates the reaction of the methylphosphine radical cation.

The second step of the proposed mechanism (see Schemes 1 and 2), nucleophilic substitution of $CH_3S^\bullet$ in the dimethyl disulfide radical cation by the neutral phosphorus compound, was demonstrated to be feasible by examining reactions of neutral trimethylphosphite and neutral trimethyl phosphine with the dimethyl disulfide radical cation. Both phosphorus compounds readily replace $CH_3S^\bullet$ in the dimethyl disulfide radical cation (Scheme 3; trimethylphosphine: 76% $CH_3S^\bullet$ replacement at 0.6 efficiency; trimethyl phosphite: 100% $CH_3S^\bullet$ replacement at 0.6 efficiency). In the case of trimethylphosphine, neutralization of the dimethyl disulfide radical cation by charge exchange is slightly exothermic ($\Delta H_{\mathrm{rxn}} \approx -1$ kcal/mol) and hence able to compete with the replacement reaction (24% of the product distribution arises from charge exchange).

Neutral methylphosphine was also found to react with the dimethyl disulfide radical cation by replacement of $CH_3S^\bullet$ albeit at a low efficiency. This finding demonstrates that if a long-lived collision complex of neutral methylphosphine and the radical cation of dimethyl disulfide were generated upon reaction of the radical cation of methylphosphine and neutral dimethyl disulfide, $CH_3S^\bullet$ abstraction would have been observed. It is concluded that the high exothermicity associated with neutralization of the phosphorus radical cation by dimethyl disulfide must make the lifetime of the resulting complex very short, preventing further reactions within the neutral and ionic product.

Finally, some support for the proposed $CH_3X^\bullet$ abstraction mechanism (X = S, Se) is also obtained from the very high rate constants measured for the abstraction reactions (efficiencies range from 0.4 up to 1.0; Table 1). The high reaction rates preclude the radical substitution mechanism[15] thought to apply to the reaction of distonic radical cations[1] with dimethyl disulfide since the latter reactions occur slowly (the efficiencies are usually in the order of 0.05).[1,3,4,9] However, charge exchange involving organic radical cations is often facile in the gas phase (e.g., see Table 1).[16] Further, nucleophilic substitution of $CH_3S^\bullet$ in the dimethyl disulfide radical cation by neutral trimethylphosphine and trimethyl phosphite was demonstrated in this study to be a very efficient reaction. Thus, if $CH_3S^\bullet$ and $CH_3Se^\bullet$ abstraction by the trimethylphosphine and trimethyl phosphite radical cations occurs by the proposed mechanism, the reaction rates would be expected to be high.

The above results suggest that conventional organophosphorus radical cations with recombination energies close to the ionization energy of dimethyl disulfide and dimethyl diselenide react with these reagents via a two-step mechanism generating $CH_3X^\bullet$ abstraction products (X = S, Se). However, it is important to note that *not all* conventional radical cations with recombination energies close to 8.0 eV react this way. For example, conventional radical cations with nitrogen and sulfur functionalities react with dimethyl disulfide and dimethyl diselenide by exclusive charge exchange even when their recombination energies are 7.8−8.5 eV, e.g., the radical cations of aniline, 3,4-dihydro-2*H*-pyran and ethyl methyl sulfide.[4,13a,14] Therefore, the behavior exhibited by the trimethylphosphine and trimethyl phosphite radical cations is a function of not only their recombination energies but also the nucleophilicity of the phosphorus atom. In fact, quite parallel reactivity has been reported earlier for neutral triphenylphosphine, $(C_6H_5)_3P$, in solution.[17] This phosphine reacts with neutral disulfides (RSSR) by nucleophilic substitution of RS^- to intially produce $(C_6H_5)_3P^+{-}SR$; a further reaction with RS^- yields RSR and $(C_6H_5)_3PS$ as the final products.[17]

Conclusions

Conventional radical cations with oxygen, nitrogen, and sulfur functionalities are known to react with dimethyl disulfide and dimethyl diselenide by charge exchange or to be unreactive.[1,3,4] In sharp contrast, the radical cations of trimethylphosphine and trimethyl phosphite react with these reagents by $CH_3X^\bullet$ abstraction (X = S, Se). These abstraction reactions have been previously reported only for distonic radical cations. However, the conventional organophosphorus radical cations do not isomerize to their distonic forms *prior to* or during the reaction

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[15] Poutsma, M. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973.

[16] Han, C.-C.; Wilbur, J. L.; Brauman, J. I. *J. Am. Chem. Soc.* **1992**, *114*, 887.

[17] See, for example: Burns, J. A.; Butler, J. C.; Moran, J.; Whitesides, G. M. *J. Org. Chem.* **1991**, *56*, 2648.

since the connectivity of the radical cation is retained throughout the reaction.

A two-step mechanism is proposed to rationalize the reactivity of trimethylphosphine and trimethyl phosphite radical cations. Near-thermoneutral charge exchange likely initiates the reaction, leading to a long-lived ion−molecule complex. Within this complex, nucleophilic attack by the neutral phosphorus compound at the radical cation of dimethyl disulfide or dimethyl diselenide generates the observed ionic product.

The replacement step is supported by the observation of facile $CH_3S^\bullet$ replacement by neutral trimethylphosphine and trimethyl phosphite when allowed to react with the dimethyl disulfide radical cation. Further, the occurrence of exclusive charge exchange between the radical cation of methylphosphine with dimethyl disulfide, inspite of the fact that the *neutral* methylphosphine reacts with the dimethyl disulfide radical cation by $CH_3S^\bullet$ replacement, demonstrates that thermoneutral charge exchange between the radical cation and dimethyl disulfide is a crucial step in the pathway leading to $CH_3X^\bullet$ abstraction.

The ability of conventional radical cations to abstract a $CH_3X^\bullet$ group (X = S, Se) from dimethyl disulfide and dimethyl diselenide seems to be limited to organophosphorus radical cations with recombination energies close to 8.0 eV. Conventional radical cations containing nitrogen and sulfur functionalities do not show similar reactivity even when their recombination energies match the ionization energy of dimethyl disulfide and dimethyl diselenide.

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