4374 *J. Am. Chem. Soc.* **1995,** *117,* 4374–4378

Reactivity of the Prototype Organosulfur Distonic Ion: $^{\bullet}CH_2SH_2^+$

Phillip K. Chou, Rebecca L. Smith, Leonard J. Chyall, and Hilkka I. Kenttämaa*

Contribution from the Department of Chemistry, Herbert C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

Received February 18, 1994®

Abstract: The intrinsic chemical properties of the prototype organosulfur distonic ion $^{\bullet}CH_2SH_2^+$ have been examined in the gas phase in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer. These studies reveal that the reactivity of the ion $^{\bullet}CH_2SH_2^+$ is quite different from that reported recently for the analogous oxygen-containing distonic ion $^{\bullet}CH_2OH_2^+$. Facile deprotonation and hydrogen atom abstraction reactions have been reported for the latter ion. However, reaction of $^{\bullet}CH_2SH_2^+$ with neutral molecules often yields the radical cation of the neutral reagent. This reaction likely occurs via deprotonation of the ion followed by other reactions within the collision complex. Collisions with neutral reagents with ionization energies ≥ 9.9 eV can result in base-catalyzed isomerization of the distonic ion to the more stable conventional isomer $CH_3SH^{\bullet+}$. The isomerization is revealed by curved kinetics plots and, at long reaction times, by product ions identical to those observed for the conventional isomer. At short reaction times, however, the reactivity of the unrearranged distonic ion can be probed. Examination of deprotonation reactions yields a gas-phase proton affinity of ≤ 176 kcal mol^{-1} for $^{\bullet}CH_2SH$ at the sulfur atom. In combination with the known heats of formation of H^+ and $^{\bullet}CH_2SH$, the new proton affinity value yields a lower limit of 227 kcal mol^{-1} for the heat of formation of $^{\bullet}CH_2SH_2^+$. This value is higher than the previously reported experimental value (219 kcal mol^{-1}).

Introduction

Distonic radical cations characterized by spatially separated charge and radical sites have been of considerable interest since the discovery that the ion $^{\bullet}CH_2OH_2^+$ is more stable than its conventional isomer, $CH_3OH^{\bullet+}$.[1] Distonic ions play a central role in many chemical transformations. Gas-phase[2a–c,f] as well as condensed-phase[3] experiments have been used to explore their formation and reactivity. However, most of these studies are limited to oxygen- and nitrogen-containing species. Indeed, very little is currently known about the chemical properties of distonic ions containing second-row elements.[2c–f]

Sulfur-containing distonic ions are especially intriguing species. In contrast to many other distonic ions, the simple organosulfur distonic ions have been predicted[2,4] to be *less stable* than their conventional isomers. Therefore, these ions might show quite different chemical properties than the analogous oxygen-containing ions that are thermodynamically stable (e.g., $^{\bullet}CH_2OH_2^+$ and $^{\bullet}CH_2CH_2OH_2^+$).[2,5] Gas-phase studies on the reactivity of organosulfur distonic ions are currently limited to the ion $(CH_3)_2S^+CH_2^{\bullet}$.[4b,c,6] This ion is less stable than its conventional isomer, the radical cation of ethyl methyl sulfide, but it is kinetically stable toward isomerization.[4b,c,6] We report here the first investigation of the bimolecular reactions of the prototype organosulfur distonic ion $^{\bullet}CH_2SH_2^+$. This ion has a more stable *tautomeric* form, $CH_3SH^{\bullet+}$.[2f,7–9]

Bouma *et al.* have demonstrated the formation of $^{\bullet}CH_2SH_2^+$ upon fragmentation of ionized 2-mercaptoethanol (eq 1).[7] The

$$HOCH_2CH_2SH \xrightarrow{-e^-} [HOCH_2CH_2SH]^{+\bullet} \xrightarrow{-CH_2O} {}^{\bullet}CH_2SH_2^+ \qquad (1)$$

distonic ion was differentiated from its conventional isomer, the radical cation of methanethiol ($CH_3SH^{\bullet+}$), on the basis of differences in collision-activated dissociation products.[7] The distinct nature of these two species was later confirmed by Terlouw *et al.*[8] Using appearance energy measurements, the latter workers determined a heat of formation of 219 kcal mol^{-1} for $^{\bullet}CH_2SH_2^+$,[9] a value 6.7 kcal mol^{-1} greater than the heat of formation of $CH_3SH^{\bullet+}$ (212.3 kcal mol^{-1}).[10a] A much greater energy difference (18.8 kcal mol^{-1}; $\Delta H_f(CH_3SH^{\bullet+}) = 213.4$ kcal/mol; $\Delta H_f(^{\bullet}CH_2SH_2^+) = 232.2$ kcal/mol) was later reported by Radom and co-workers, who used high-level G2′ *ab initio* molecular orbital calculations to examine the relative stabilities of the isomers.[4a] The source for the discrepancy was suggested to lie in the possibly inaccurate ΔH_f used for 2-mercaptoethanol; an erroneous value would affect the energy difference obtained from the appearance energy measurements.[4a]

Our study demonstrates that the long-lived ion $^{\bullet}CH_2SH_2^+$ is chemically distinct from ionized methanethiol. However, certain

---

® Abstract published in *Advance ACS Abstracts,* March 15, 1995.

[1] (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2929. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2930. (c) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 2931.

[2] (a) Stirk, K. M.; Kiminkinen, M.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649. (b) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (c) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225. (d) Pius, K.; Chandrasekhar, J. *Int. J. Mass Spectrom. Ion Processes* **1989**, *87*, R15. (e) Srinivas, R.; Böhme, D. K.; Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1939. (f) Maquin, F.; Stahl, D.; Sawaryn, A.; von R. Schleyer, P.; Koch, W.; Frenking, G.; Schwarz, H. *J. Chem. Soc., Chem. Commun.* **1984**, 504.

[3] Symons, M. C. R. *Chem. Soc. Rev.* **1984**, 393.

[4] (a) Gauld, J. W.; Radom, L. *J. Phys. Chem.* **1994**, *98*, 777. (b) Smith, R. L.; Chyall, L. J.; Stirk, K. M.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1993**, *28*, 1623. (c) Chyall, L. J.; Byrd, M. H. C.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1994**, *116*, 10767. (d) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805.

[5] (a) Stirk, K. G.; Kenttämaa, H. I. *J. Phys. Chem.* **1992**, *96*, 5272. (b) Mourgues, P.; Audier, H. E.; Leblanc, D.; Hammerum, S. *Org. Mass Spectrom.* **1993**, *28*, 1098.

[6] van Amsterdam, M. W.; Staneke, P. O.; Ingemann, S.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1993**, *28*, 919.

[7] Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1982**, *104*, 2931.

[8] Terlouw, J. K.; Heerma, W.; Dijkstra, G.; Holmes, J. L.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *47*, 147.

[9] Holmes, J. L.; Lossing, F. P.; Terlouw, J. K.; Burgers, P. C. *Can. J. Chem.* **1983**, *61*, 2305.

0002-7863/95/1517-4374$09.00/0

bases catalyze isomerization of the distonic ion to the more stable conventional isomer. Further, $^{\bullet}CH_2SH_2^+$ reacts with many neutral molecules through a pathway that formally corresponds to electron transfer, a reaction not commonly observed for small distonic ions.[2,5,6] Finally, examination of the deprotonation reactions of $^{\bullet}CH_2SH_2^+$ suggests that the previously reported experimental ΔH_f value is too low.

Experimental Section

The experiments were carried out using an Extrel Model 2001 Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR) that has been described elsewhere.[11] The instrument contains two 4.7 cm cubic cells (dual cell) that are differentially pumped and housed within a 3 T superconducting magnet.

A typical experiment consists of formation of ions in one side of the dual cell, transfer into the other cell, collisional cooling, isolation of the desired ion, time delay for reactions, and detection. Primary ions were formed by 20 or 70 eV electron ionization of appropriate neutral precursors (2-mercaptoethanol for the distonic ion; methanethiol for the conventional ion). The ionization conditions (25−50 ms ionization time, 4−8 μA filament current) were optimized for each experiment. Ions were trapped by applying a potential of +2.0 V to the three cell plates perpendicular to the magnetic field lines. After generation in one side of the dual cell, the ions were transferred into the other cell through a 2 mm hole in the trapping plate common for the two cells by temporarily grounding this plate (100−200 μs). Argon was pulsed into the cell (up to 1×10^{-5} Torr) and the ions were cooled by multiple collisions (≥50) with argon, as described earlier.[11] No endothermic reactions are generally observed for long-lived organic ions treated this way.[11e,f] Isolation of the desired ion was achieved by ejecting unwanted ions from the cell through the application of appropriate excitation pulses to the cell plates. The ions were then allowed to react for a variable time period with a neutral reagent introduced into the cell through a leak valve or a set of pulsed valves. Ions were excited for detection by using a stored waveform inverse Fourier-transform waveform (Extrel FTMS SWIFT module).[12] All reagents except one[13] were commercially available and used as received. Their purity was checked by mass spectrometry.

Results and Discussion

The distonic ion $^{\bullet}CH_2SH_2^+$ (generated by electron ionization of 2-mercaptoethanol as described in the Experimental Section) was expected to act as a strong Brønsted acid in most of its reactions, analogous to the behavior of the ion $^{\bullet}CH_2OH_2^+$.[5b] Based on $\Delta H_f(^{\bullet}CH_2SH) = 37$ kcal mol^{-1},[14] and the earlier estimates for the heat of formation of $^{\bullet}CH_2SH_2^+$ (219−232 kcal mol^{-1}),[4a,c,9] a proton affinity of 171−185 kcal mol^{-1} was predicted for the sulfur atom in $^{\bullet}CH_2SH$. Therefore, proton transfer was expected to be the dominant reaction pathway for reaction of $^{\bullet}CH_2SH_2^+$ with molecules with proton affinities greater than 185 kcal mol^{-1}. However, when the ion was allowed to react with strong bases, the only product observed in most cases was *the radical cation* of the neutral reagent (Table 1; the reaction efficiency or $k_{observed}/k_{collision}$ was ≥0.5 for all these reactions except for that of CH_3I). This result was unexpected for two reasons. First, proton transfer is generally facile in the gas phase if exothermic and therefore should have been observed.[16] Second, electron transfer is not expected for $^{\bullet}CH_2SH_2^+$ because a high-energy species, a sulfur ylide,[17] would be formed as the neutral product (eq 2). Indeed, no electron transfer reactions have been observed for the higher homolog $(CH_3)_2S^+{-}CH_2^{\bullet}$.[4b,6]

Table 1. Ion/Molecule Reactions of $^{\bullet}CH_2SH_2^+$ with Neutral Reagents with Ionization Energies (IE) ≤9.5 eV

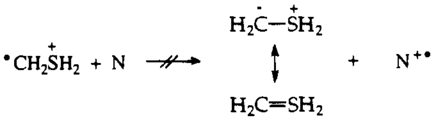
reagent	PA (kcal mol^{-1})[a]	IE (eV)[a]	reaction
aniline	209.5	7.72	charge exchange
cyclopentanone	198.8	9.24	proton transfer
dimethyl disulfide	≈196	8.0[b]	charge exchange
thiophene	195.8	8.87	charge exchange
1,4-dioxane	193.8	9.2	charge exchange
furan	192.2	8.8	charge exchange
toluene	187.7[c]	8.82	charge exchange
benzene	180.0[c]	9.25	charge exchange
methyl iodide	171	9.5	slow charge exchange

[a] Reference 10b. [b] Reference 14. [c] Reference 10c.

Table 2. Ion/Molecule Reactions of $CH_3SH^{\bullet+}$ (Recombination Energy[10b] 9.44 eV) with Various Neutral Reagents

reagent	PA (kcal mol^{-1})[a]	IE (eV)[a]	reaction
aniline	209.5	7.72	charge exchange
cyclopentanone	198.8	9.24	charge exchange
acetic acid	190.2	10.66	proton transfer
toluene	187.7[b]	8.82	charge exchange
methanol	181.7	10.85	proton transfer
benzene	180.0[b]	9.25	charge exchange
formic acid	178.8[b]	11.33	methyl cation transfer
trichloroacetonitrile	175.8	11.89	no reaction

[a] Reference 10b. [b] Reference 10c.



$$^{\bullet}CH_2\overset{+}{S}H_2 + N \not\longrightarrow \left[H_2\dot{C}{-}\overset{+}{S}H_2 \leftrightarrow H_2C{=}SH_2 \right] + N^{+\bullet} \qquad (2)$$

Isomerization of the distonic ion $^{\bullet}CH_2SH_2^+$ to the conventional ion $CH_3SH^{\bullet+}$ by an intramolecular 1,2-hydrogen atom shift prior to reaction could conceivably account for the observed reactivity. Given the recombination energy of $CH_3SH^{\bullet+}$ (9.44 eV[10b]) and those of the neutral reagents studied,[10] electron transfer involving $CH_3SH^{\bullet+}$ would be highly exothermic. Indeed, charge exchange was found to be the exclusive channel for the reaction of $CH_3SH^{\bullet+}$ with reagents such as toluene and aniline (Table 2; the reactions occur at collision rate). However, several pieces of evidence show that $^{\bullet}CH_2SH_2^+$ has *not* isomerized to $CH_3SH^{\bullet+}$ prior to reaction. For example, the

---

(10) (a) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data (Suppl. 1)* **1977**, *6*. (b) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data (Suppl. 1)* **1988**, *17*. (c) Szulejko, J. E.; McMahon, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 7839.

(11) (a) Stirk, K. M.; Smith, R. L.; Orlowski, J. C.; Kenttämaa, H. I. *Rapid Commun. Mass Spectrom.* **1993**, *7*, 392. (b) Zeller, L.; Farrell, J., Jr.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 1205. (c) Stirk, K. G.; Kenttämaa, H. I. *J. Phys. Chem.* **1992**, *96*, 5272. (d) Farrell, J. T., Jr.; Lin, P.; Kenttämaa, H. I. *Anal. Chim. Acta* **1991**, *246*, 227. (e) Lin, P.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1992**, *27*, 1155. (f) Leeck, D. T.; Stirk, K. M.; Zeller, L. C.; Kiminkinen, L. K.; Castro, L. M.; Vainiotalo, P.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1994**, *116*, 3028.

(12) Chen, L.; Wang, T.-C. L.; Ricca, T. L.; Marshall, A. G. *Anal. Chem.* **1987**, *59*, 449.

(13) 2-Mercaptoethanol was partially deuterated by stirring a mixture of $HSCH_2CH_2OH$ (1 equiv) and D_2O (10 equiv) overnight under an atmosphere of nitrogen. Subsequently, the mixture was extracted with diethyl ether and the collected organic fractions dried with anhydrous $MgSO_4$. The ether was removed under reduced pressure (about 20 mmHg). Electron ionization mass spectrum measured for the resulting compound indicated that most of the gaseous $HSCH_2CH_2OH$ molecules inside the mass spectrometer contained one deuterium atom. The fragment ion of *m/z* 49 ($^{\bullet}CH_2SHD^+$) was isolated for further studies.

(14) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1992**, *97*, 1818.

(15) Leeck, D. T.; Kenttämaa, H. I. *Org. Mass Spectrom.* **1994**, *29*, 106.

(16) Bartmess, J. E.; McIver, R. T., Jr. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.

(17) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1987**, *109*, 1: ΔH_f value calculated for $CH_2{=}SH_2$ yields IE = 6.8 eV for $CH_2{=}SH_2$ if ΔH_f = 232 kcal/mol is used for $^{\bullet}CH_2SH_2^+$ (ref 4a). A value calculated by us using ab initio molecular orbital theory at the HF/6-31+G(d) level yields IE = 6.9 eV. Hence, electron transfer to $^{\bullet}CH_2SH_2^+$ to yield $CH_2{=}SH_2$ cannot occur for the reagents studied.

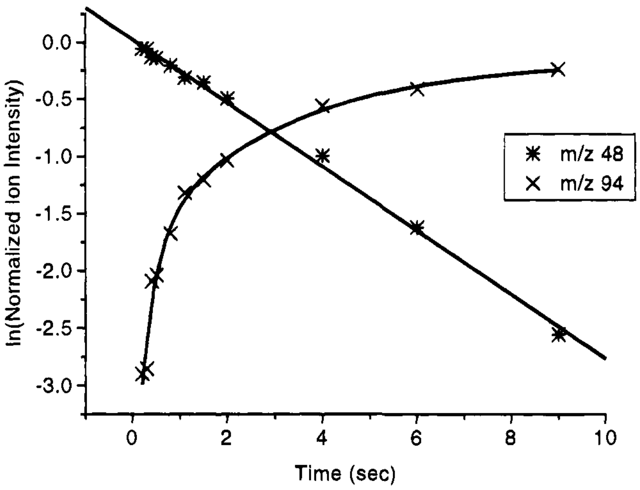


Figure 1. Temporal variation of the abundance of the ion $^{\bullet}CH_2SH_2^+$ (*m/z* 48) upon reaction with dimethyl disulfide. The line is the least-squares fit.

reaction rates of the two isomers are different, the electron transfer reactions involving $CH_3SH^{\bullet +}$ occurring approximately twice as efficiently as those of $^{\bullet}CH_2SH_2^+$. In some instances, different reaction products (discussed later in this paper) are formed for the two isomers, further demonstrating that the ion $^{\bullet}CH_2SH_2^+$ is distinct from $CH_3SH^{\bullet +}$. The plots of the natural logarithm of the signal of $^{\bullet}CH_2SH_2^+$ as a function of reaction time appear linear and the reactions go to completion (shown for reaction with dimethyl disulfide in Figure 1), suggesting that the reactant ion population is not likely to have a large proportion of the conventional ions among the distonic ions, *i.e.*, $^{\bullet}CH_2SH_2^+$ has not partially isomerized to $CH_3SH^{\bullet +}$ prior to collision with the neutral reagent.

Isomerization of $^{\bullet}CH_2SH_2^+$ by an intramolecular 1,2-hydrogen atom shift *within the collision complex* prior to reaction cannot be ruled out on the basis of experimental results alone. However, molecular orbital calculations carried out by others[4c] suggest that a 1,2-H shift in $^{\bullet}CH_2SH_2^+$ to yield $CH_3SH^{\bullet +}$ has a very high energy barrier (over 45 kcal mol^{-1}). The ion–molecule complexation energy alone (typically 10–20 kcal mol^{-1}) is not sufficient to overcome this energy barrier.

The above discussion suggests that unimolecular isomerization of $^{\bullet}CH_2SH_2^+$ to $CH_3SH^{\bullet +}$ is not likely to occur prior to reaction of $^{\bullet}CH_2SH_2^+$ with the neutral reagents studied. Hence, the formal charge exchange reaction of $^{\bullet}CH_2SH_2^+$ is best explained by involving an intermolecular H^+-transfer within the ion–molecule collision complex, as outlined in Scheme 1.[18] The approximate enthalpy changes associated with the different steps for the reaction with toluene are illustrated in Figure 2a. Proton transfer to toluene is expected to be exothermic by more than 10 kcal mol^{-1} (Figure 2a) and to occur readily. The resulting products (**II**, Scheme 1) do not separate to yield $^{\bullet}CH_2SH$ and protonated toluene but undergo another exothermic reaction. Two channels are accessible for this collision complex: hydrogen atom transfer (**II** → **V**, Scheme 1) and proton transfer (**II** → **III**, Scheme 1). On thermodynamic grounds (Figure 2a), hydrogen atom transfer is expected to be the most likely pathway ($\Delta H_{\text{reaction}} = -16$ kcal mol^{-1}).[10,13] However, the two possible pathways cannot be experimentally distinguished. If proton transfer occurs between $^{\bullet}CH_2SH$ and protonated toluene (**II** → **III**), it is almost certainly followed by fast exothermic electron transfer (**III** → **V**, Scheme 1; $\Delta H_{\text{reaction}} = -15$ kcal mol^{-1}; Figure 2a) or, less likely, by proton transfer followed by hydrogen atom transfer (**III** → **IV** → **V**). These processes yield the same final products as the hydrogen atom transfer reaction (**II** → **V**, Scheme 1): ionized toluene and CH_3SH.

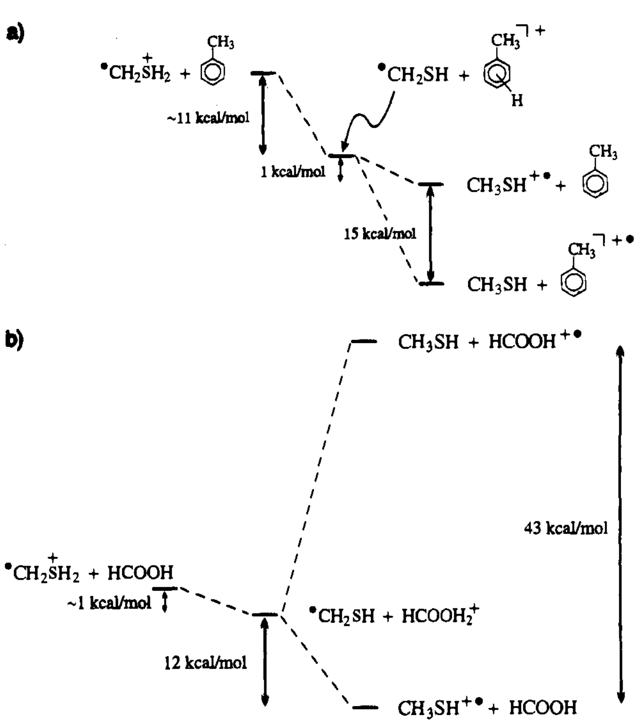
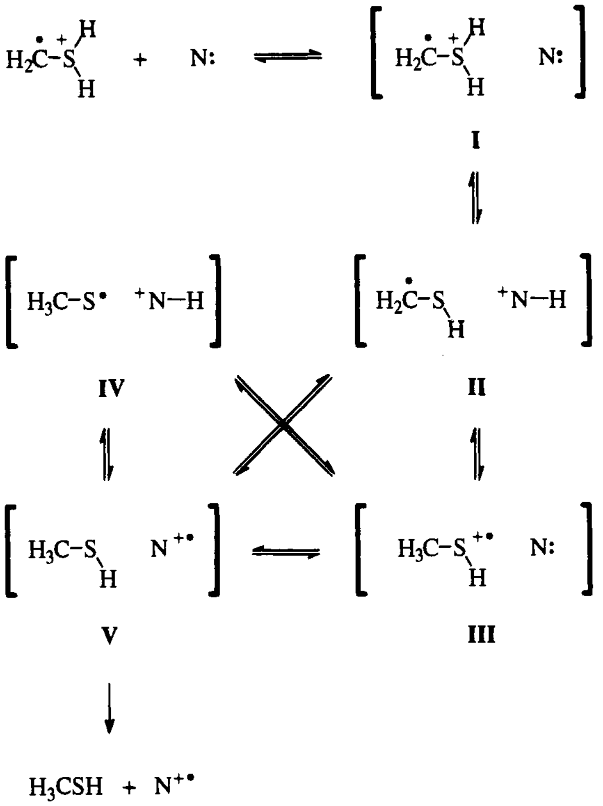


Figure 2. Approximate enthalpy changes[9,10] for the reactions occurring within the collision complex of $^{\bullet}CH_2SH_2^+$ with (a) toluene and (b) formic acid.

Scheme 1



The proposal that the formal charge exchange reactions of $^{\bullet}CH_2SH_2^+$ occur via proton transfer to the neutral reagent is supported by the results obtained for the reaction of aniline with the partially deuterium labeled ion $^{\bullet}CH_2SHD^+$.[13] This reaction yields ionized aniline as well as ionized aniline-d_1 as the product

---

[18] (a) Bohme, D. K. *Int. J. Mass Spectrom. Ion Processes* **1992**, *115*, 95. (b) See also: Audier, H. E.; Leblanc, D.; Mourques, P.; McMahon, T. B.; Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2329.

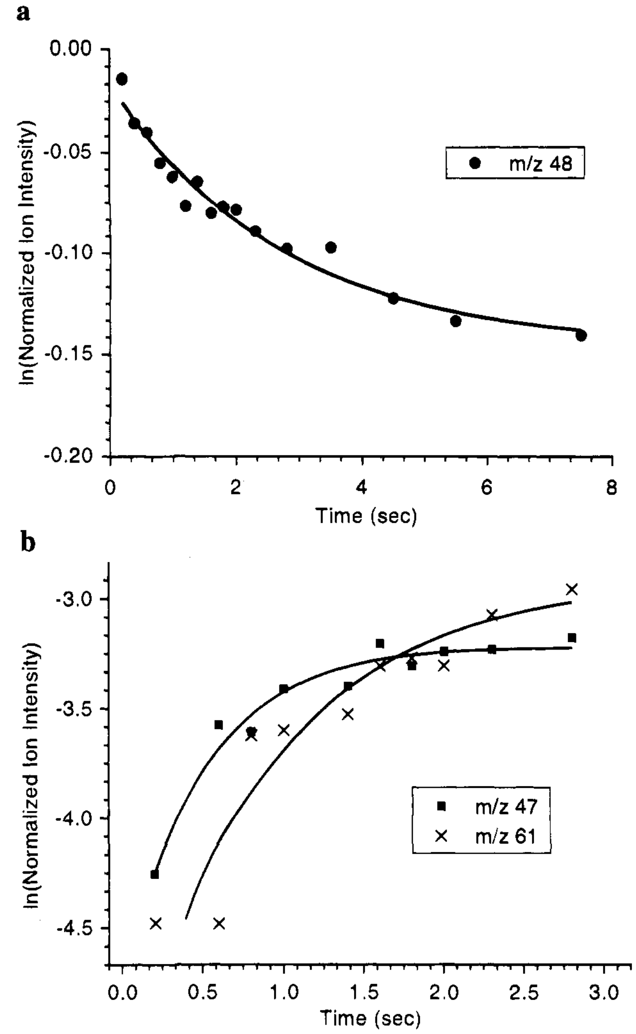


Figure 3. Temporal variation of the abundance of (a) the reactant ion $^{\bullet}CH_2SH_2^+$ (*m/z* 48) and (b) the product ions $HC(OH)_2^+$ (*m/z* 47) and $HC(OH)OCH_3^+$ (*m/z* 61) for the reaction with HCOOH. The lines are arbitrary smooth curves drawn through the data points.

ions, demonstrating that exchange of the hydrogen atoms of the ion and aniline must have occurred during the reaction. The facile occurrence of H/D-exchange within the collision complexes of $^{\bullet}CH_2SH_2^+$ is further demonstrated by the finding that collisions with CD_3OD lead to sequential exchange of all the hydrogen atoms of $^{\bullet}CH_2SH_2^+$ with deuterium atoms. A similar process occurs for the conventional ion, possibly via the intermediates **II**, **IV**, and **V** shown in Scheme 1.

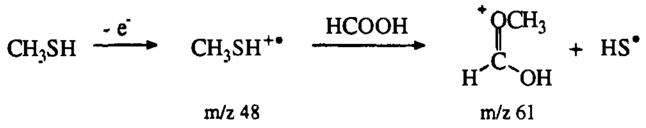
Ionization of a neutral reagent by $^{\bullet}CH_2SH_2^+$ as shown in Scheme 1 apparently becomes inaccessible for reagents with ionization energies greater than 9.5 eV since $^{\bullet}CH_2SH_2^+$ ionizes CH_3I (IE = 9.5 eV; Table 1) only very slowly and does not ionize reagents with higher ionization energies (Table 3). The distonic ion reacts with acetic acid, methanol, and formic acid by the expected proton transfer, yielding $CH_3C(OH)_2^+$, $CH_3OH_2^+$, and $HC(OH)_2^+$, respectively (Table 3; see Figure 2b for the energetics of the reaction with formic acid, IE = 11.33 eV). However, in some instances, proton transfer is accompanied by base-catalyzed isomerization of $^{\bullet}CH_2SH_2^+$ to the conventional isomer (**I** → **II** → **III** in Scheme 1; dissociation of **III** leads to the products; see also Figure 2b). The isomerization is readily apparent from the nonlinear decay of the semilogarithmic plot of the reactant ion signal as a function of time for the reaction with formic acid (Figure 3a), indicating the presence of two isomeric ions reacting at different rates. Proton transfer is observed only at short reaction times, before collisions with formic acid have converted all the $^{\bullet}CH_2SH_2^+$ ions to $CH_3SH^{\bullet+}$. A new product ion, methylated formic acid (*m/z* 61), appears at longer reaction times. The formation of this product ion unambiguously demonstrates the presence of $CH_3SH^{\bullet+}$ at longer reaction times: authentic $CH_3SH^{\bullet+}$ also reacts with formic acid by methyl cation transfer (Scheme 2; Table 2).

Table 3. Ion/Molecule Reactions of $^{\bullet}CH_2SH_2^+$ with Neutral Reagents with Ionization Energies (IE) ≥9.9 eV

reagent	PA (kcal mol^{-1})[a]	IE (eV)[a]	reaction
acetic acid	190.2	10.66	proton transfer
methanol	181.7	10.85	proton transfer
formic acid	178.8[b]	11.33	proton transfer methyl cation transfer
trichloroacetonitrile	175.8	11.89	no reaction
malononitrile	175.6	12.7	no reaction
1,1,1-trifluoroacetone	173.5[b]	10.67	no reaction
hydrogen sulfide	168.7[b]	10.45	no reaction
hexafluorobenzene	153.8[b]	9.91	no reaction

[a] Reference 10b. [b] Reference 10c.

Scheme 2



Scheme 3

$$^{\bullet}CH_2SH + H^+ \longrightarrow {}^{\bullet}CH_2\overset{+}{S}H_2 \qquad \Delta H_{rxn} = -PA({}^{\bullet}CH_2SH)$$

$$\Delta H_f({}^{\bullet}CH_2\overset{+}{S}H_2) = -PA({}^{\bullet}CH_2SH) + \Delta H_f(H^+) + \Delta H_f({}^{\bullet}CH_2SH)$$

The different reactivity of the ions $^{\bullet}CH_2SH_2^+$ and $CH_3SH^{\bullet+}$ demonstrates that these ions are distinct at short reaction times. The conventional ion $CH_3SH^{\bullet+}$ is not sufficiently acidic to protonate the weakest bases used in this study: the proton affinity of $CH_3S^{\bullet}$ is 184.8 kcal mol^{-1} and that of $^{\bullet}CH_2SH$ at the carbon atom is 191.1 kcal mol^{-1}.[13] However, the ion $^{\bullet}CH_2SH_2^+$ protonates formic acid but not molecules with proton affinities below 176 kcal mol^{-1} (Table 2). This finding suggests that the proton affinity of the sulfur atom in $^{\bullet}CH_2SH$ is 175.8–178.8 kcal mol^{-1}. However, since the competing isomerization of $^{\bullet}CH_2SH_2^+$ to $CH_3SH^{\bullet+}$ may dominate a thermoneutral or even slightly exothermic proton transfer, the value 176 kcal mol^{-1} should be considered as the upper limit for the proton affinity. An estimated proton affinity of ≤176 kcal mol^{-1} for the sulfur atom in $^{\bullet}CH_2SH$ and the known[10b,14] heats of formation of 37 kcal mol^{-1} for $^{\bullet}CH_2SH$ and 365.7 kcal mol^{-1} for H^+ yield (Scheme 3) a heat of formation of ≥227 kcal mol^{-1} for $^{\bullet}CH_2SH_2^+$.

Conclusions

The prototype organosulfur distonic ion $^{\bullet}CH_2SH_2^+$ has been previously shown to be stable toward unimolecular isomerization to the more stable ion $CH_3SH^{\bullet+}$.[7,8] The present study demonstrates that access to a more stable tautomeric form nevertheless greatly influences the outcome of the reactions of $^{\bullet}CH_2SH_2^+$. Molecules with ionization energies ≤9.5 eV are ionized by the distonic ion in a reaction which most likely involves a facile proton/hydrogen atom exchange, yielding methanethiol as the neutral product. This type of reactivity has not been observed for the analogous oxygen-containing distonic ions (e.g., $^{\bullet}CH_2OH_2^+$) that are thermodynamically stable.[2,5] Neutral molecules with relatively high ionization energies can induce base-catalyzed isomerization of the distonic ion to $CH_3SH^{\bullet+}$. Examination of the deprotonation reactions of the unrearranged distonic ion yields a proton affinity of ≤176 kcal mol^{-1} for the sulfur atom in $^{\bullet}CH_2SH$, and a lower limit of 227 kcal mol^{-1} for the heat of formation of $^{\bullet}CH_2SH_2^+$. This value is closer to the heat of formation obtained by recent high-level *ab initio* molecular orbital calculations[4a] (232 kcal mol^{-1}) than the previous experimental value[9] (219 kcal mol^{-1}).

Acknowledgment. The National Science Foundation (CHE-9409644), the donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the Lubrizol Corporation are acknowledged for financial support.

JA940539V