

Radical-Type Reactivity of the Methylenedimethylsulfonium Ion, $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$

Rebecca L. Smith, Leonard J. Chyall, Krista M. Stirk and Hilikka I. Kenttämäa*

Department of Chemistry, Brown Building, Purdue University, West Lafayette, Indiana 47907-1393, USA

Ab initio molecular orbital calculations at the MP2/6-31G**//6-31G* + ZPVE level of theory suggest that the ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ is 75 kJ mol⁻¹ higher in energy than ionized ethyl methyl sulfide. However, this distonic ion is stable toward isomerization to the conventional structure: the two ions show distinctly different reactivity in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer. Molecular orbital calculations further indicate that the charge site of the ion is on the sulfur atom whereas the odd-spin density is localized on the CH₂ group. The chemical properties of the ion reflect this description. The coordinatively saturated sulfonium charge site is chemically inert. This radical cation possesses unique chemical reactivity in that its reactions are associated with the radical site. Most of these reactions involve a homolytic bond cleavage in the neutral molecule, resulting in abstraction of an atom or a radical by the ion. The reaction efficiency correlates with the homolytic bond dissociation energy of the bond being broken in the neutral molecule, suggesting a simple radical abstraction mechanism for these reactions. Hence, the methylenedimethylsulfonium ion is best described as an electrophilic radical with an inert charge site.

INTRODUCTION

Since the discovery in 1984 that radical cations with spatially separate charge and radical sites (distonic ions) can be more stable than their conventional counterparts,^{1,2} much effort has been directed into the generation and characterization of these ions. Distonic ions can potentially undergo ionic as well as radical reactions.³ Both types of reactivity have been observed.³⁻⁷ For example, the distonic ion $^\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ (generated by the loss of formaldehyde from ionized 1,4-dioxane)²⁻⁴ reacts with dimethyl disulfide by dissociative charge exchange and by abstraction of a thiomethyl radical.^{5,6} This latter reaction has proved to be useful in the structural characterization of radical cations: thiomethyl abstraction from dimethyl disulfide is common for distonic ions but does not occur for even-electron ions or conventional radical cations.⁶ Therefore, observation of this reaction provides evidence for a distonic reactant ion.

It has been proposed that distonic ions with a chemically inert charge site might provide a means to study gas-phase radical chemistry by using mass spectrometry.⁸ While most distonic ions indeed undergo radical type reactions with selected neutral reagents, the charge site is thought to participate in many of the reactions which formally take place at the odd-spin site. For example, most of the reactions of the thoroughly studied⁹⁻¹² ion $^\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ apparently occur^{3,8,11,12} via initial addition of the attacking nucleophile to the unsaturated charged center, followed by a radical reaction.

A novel sulfur-containing distonic ion, the methyl-

enedimethylsulfonium ion, $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ (*m/z* 76), was recently synthesized in the gas phase.^{6,13,14} This ion contains a coordinatively saturated charge site and cannot form an additional bond with a neutral reagent molecule. In our initial report of the synthesis of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$, we demonstrated that this ion nevertheless reacts with dimethyl disulfide to give a sole product which corresponds to abstraction of a thiomethyl radical.⁶ We report here a general survey of the bimolecular reactivity of this ion. Unlike the distonic ions studied previously,^{3,5,12} all the reactions of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ appear to be associated with the odd-spin site.

EXPERIMENTAL

All reagents were obtained commercially and checked for purity by gas chromatography and mass spectrometry. The reagents were used as received except for cyclohexa-1,4-diene, which was purified by preparative GC using a 12 ft × 4 mm i.d. (1 ft = 0.305 m) column packed with 10% OV-101 on 60-80-mesh Chromosorb W NAW to remove any contamination from cyclohexa-1,3-diene.

The experiments were carried out using an Exrel Model 2001 Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer, which has been described in detail earlier.^{5-7,12,15} The instrument consists of a differentially pumped dual cell which is aligned collinearly with a 2.3 T magnetic field produced by a 3 T superconducting magnet. The base pressure in this instrument is < 10⁻⁹ Torr (1 Torr = 133.3 Pa) which is

maintained by two Balzers (330 ls^{-1}) turbomolecular pumps, each backed by an Alcatel 2012 mechanical pump. A common wall (the conductance limit) separates the two cells. By grounding this wall, ions can be transferred from one cell into the other through a 2 mm hole in the center of the wall. At all other times, this plate and the other two trapping plates perpendicular to the magnetic field were kept at +2 V.

Samples were introduced into the FT-ICR system by two heated Extrel-manufactured single-batch inlet systems equipped with variable leak valves, or by using a Varian leak valve. Typical sample pressures were nominally 1×10^{-7} Torr, as measured by ionization gauges located on each side of the dual cell. Ions were generated by an electron beam which passes through the center of the dual cell. For each experiment, the ion signal was optimized by varying the electron energy (typically 20–30 eV), the emission current (typically 8–10 μA) and ionization time (typically 40–100 ms). The ions were transferred from the cell where they were generated into the other cell by grounding the conductance limit plate (typically for 100 μs). Before ion transfer from one cell, the other cell was cleaned free of cations generated during the electron beam by applying a negative potential (–10 V) to the trapping plate of that cell (typically for 5–10 ms). The transferred ions were internally and kinetically cooled through collisions (50–100) with argon introduced into the cell through a pulsed valve system (maximum pressure about 1×10^{-5} Torr).

After collisional cooling of the ions, the ion of interest was isolated by applying a series of single-frequency voltage pulses and radiofrequency sweeps to the excitation plates of the cell, or by the use of a SWIFT waveform¹⁶ (using Extrel FTMS SWIFT module). During isolation, care was taken to avoid excitation of the ion of interest. After the ion had been isolated, it was allowed to undergo reactions with the desired neutral reagent for a variable period of time (typically 500 ms–20 s). All of the spectra obtained are averages of at least 20 acquisitions using an excitation sweep of 107 $V_{\text{p-p}}$ amplitude, 2.7 MHz band width and either 2.2 or 124 or 3.0 kHz μs^{-1} sweep rate. The spectra were recorded as 32K data points at a digitizer rate of 5.3 MHz and subjected to one zero fill prior to Fourier transformation.

The branching ratios of product ions for each ion–molecule reaction were obtained from the relative abundances of the product ions measured at short reaction times. The slope of a plot of the logarithm of the relative abundance of the reactant ion *vs.* time was used to obtain the experimental rate constant, k_{exp} . The collision rate constant, k_{coll} , was calculated using a literature procedure.¹⁷ The total reaction efficiency is given by $k_{\text{exp}}/k_{\text{coll}}$. For rate measurements, the ion gauges were calibrated for the sensitivity¹⁸ toward each neutral reagent and for the pressure gradient between the dual cell and the ion gauge. The correction factor for the pressure gradient was obtained by measuring the rate of a reaction with a known rate constant¹⁹ involving each neutral molecule. The precision of the rate measurements for the ion–molecule reactions is better than $\pm 10\%$ and the accuracy is estimated to be better than $\pm 50\%$.

The rate constants reported for the reactions with

benzeneselenol are less accurate than those reported for the other neutral reagents because of unavailability of accurate reference data: both the dipole moment and polarizability of benzeneselenol are unknown. The dipole moment is estimated to be 1.0 D, 0.1 D lower than that of thiophenol (1.1 D), on the basis of PM3 semi-empirical calculations. The polarizability of benzeneselenol is estimated to be 14 \AA^3 by the method of Miller and Savchik.²⁰

Standard *ab initio* molecular orbital calculations were performed with the Gaussian 90 (Revision F)²¹ series of programs. Open-shell species were treated using the unrestricted Hartree–Fock (UHF) formalism.²² The geometries were fully optimized using the 6–31G* basis set.²³ Zero-point vibrational energies (ZPVE) were calculated from the 6–31G* harmonic frequencies, and scaled by a factor of 0.9 to account for the systematic overestimation of the vibrational frequencies by Hartree–Fock calculations.²⁴ Single-point calculations were carried out at the MP2/6–31G*/6–31G* + ZPVE level of theory.²⁵ The force constant matrices for the stationary points were checked to have the correct number of negative eigenvalues (zero for equilibrium structures).

RESULTS

The ion $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^*$ (m/z 76) was synthesized using several different ion–molecule reactions in the FT-ICR system. The distonic ion $^+\text{CH}_2\text{OCH}_2^+$, generated^{2,3} by electron impact ionization of ethylene oxide or 1,3-dioxolane, transfers $\text{CH}_2^{+\cdot}$ to dimethyl sulfide to yield the methylenedimethylsulfonium ion [Scheme 1(a)].^{6,14} Another method used to prepare $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^*$ involved electron impact ionization of cyclobutanone to generate¹¹ the γ -distonic ion $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ (m/z 70), which transfers¹² $\text{CH}_2^{+\cdot}$ to neutral dimethyl sulfide [Scheme 1(b)]. An ion thought to be $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^*$ has also been synthesized in our laboratory by the transfer of a CH_2 group to ionized dimethyl sulfide from neutral ketene [Scheme 1(c)].¹³ Of the three methods presented, electron impact of ethylene oxide and subsequent reaction with dimethyl sulfide yields the most abundant $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^*$ if the synthesis is carried out by using only one reaction chamber, as is the case for the experiments discussed.

The distonic ion $(\text{CH}_3)_2\text{S}^+ - \text{CH}_2^*$ was synthesized in one of the cells by using one of the above methods [for an example, see Fig. 1(a)–(c)], transferred into the other cell and collisionally cooled with argon. The ion was then isolated [Fig. 1(d)] and allowed to undergo reactions with various neutral reagents [for isopropyl iodide, see Fig. 1(e)]. A typical plot of the temporal variation of the reactant and product ion abundances is shown in Fig. 2 for the reaction of Fig. 1(e). The primary reaction products and reaction rate constants, together with the estimated ion–molecule collision rates and the reaction efficiencies ($k_{\text{exp}}/k_{\text{coll}}$), are given for each neutral reagent in Table 1. The conventional ion $\text{CH}_3\text{CH}_2\text{SCH}_3^+$ was also allowed to react with several neutral reagents. The primary products, reaction rate constants, ion–molecule collision rates and reaction efficiencies are given in Table 2.

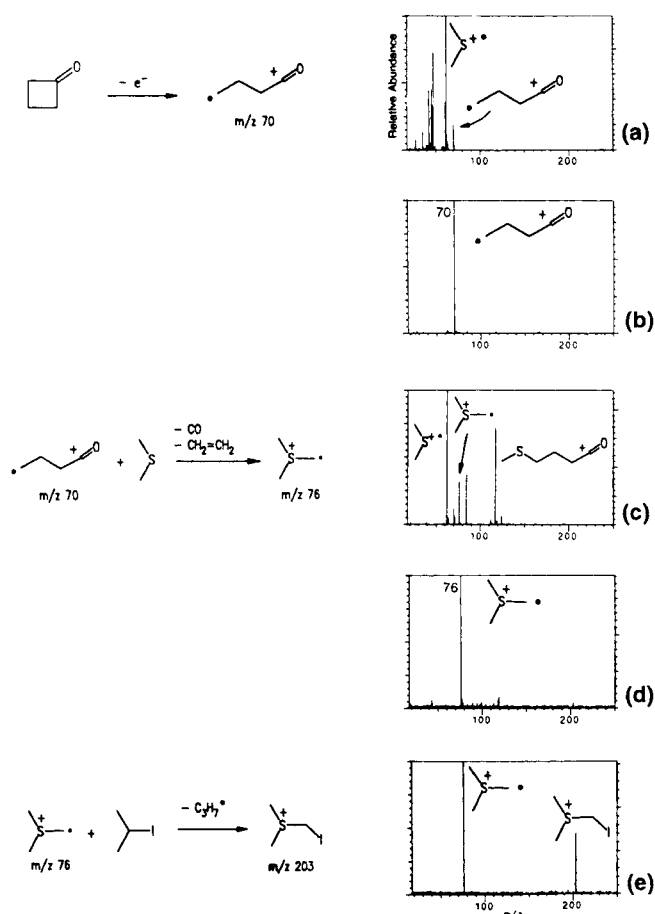
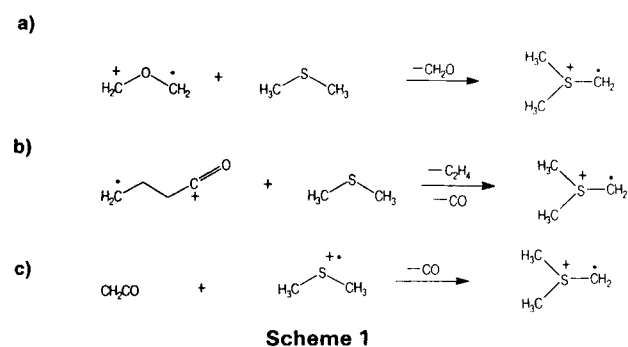


Figure 1. (a) Ionization of cyclobutanone (m/z 70). (b) Isolation of the molecular ion of cyclobutanone in one side of the dual cell. (c) Reaction of ionized cyclobutanone with dimethyl sulfide in the same side of the dual cell. (d) Transfer of the ions into the other side of the dual cell, followed by isolation of the ion of m/z 76. (e) Reaction of the ion of m/z 76 with isopropyl iodide.

Ab initio molecular orbital calculations were carried out at the MP2/6-31G**/6-31G* + ZPVE level of theory for the distonic ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ (Table 3). The calculations show that the charge site of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ is on the sulfur atom while the odd-



Scheme 1

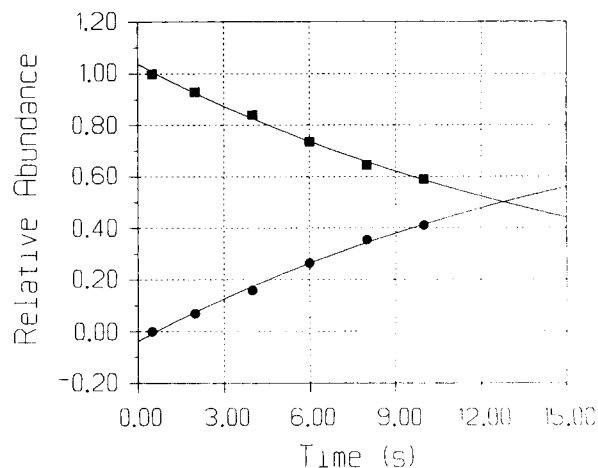


Figure 2. Plot of the reactant ion (■) and product ion (●) relative abundances as a function of time for the reaction of the methylenedimethylsulfonium ion with isopropyl iodide. The lines through the data represent the best fit to the pseudo-first-order rate equation $R_t = R_0(e^{-kt})$; $P_t = P_0 + R_0(1 - e^{-kt})$, where R_t and P_t are the reactant and product ion abundances at reaction time t , R_0 and P_0 are the initial ion abundances and k is the reaction rate constant.

spin density is localized on the CH_2 group. Several other molecules, including ionized ethyl methyl sulfide and $(\text{CH}_3)_3\text{S}^+$, were also examined computationally (see Table 3) in order to obtain a reliable estimate for the relative energies of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ and ionized ethyl

Table 1. Reactions of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ (m/z 76) with various neutral reagents

| Neutral reagent (MW) | k_{exp}^a | k_{coll}^b | $k_{\text{exp}}/k_{\text{coll}}$ | Product (m/z) | Branching ratio (%) | Reaction |
|---------------------------------|--------------------|---------------------|----------------------------------|-------------------|---------------------|------------------------------|
| Cyclohexanone (98) | — | 25 | — | — | — | No reaction |
| Trimethyl phosphite (124) | 11.2 | 16 | 0.7 | 138 | 100 | CH_2^+ transfer |
| Triethylamine (101) | 5.2 | 14 | 0.4 | 77 | 100 | H^\cdot abstraction |
| Cyclohexa-1,4-diene (80) | 1.3 | 12 | 0.1 | 77 | 56 | H^\cdot abstraction |
| | | | | 94 | 24 | CH_2^+ transfer |
| | | | | 141 | 20 | Adduct- CH_3^\cdot |
| Thiophenol (110) | 0.15 | 15 | 0.01 | 77 | 100 | H^\cdot abstraction |
| Benzeneselenol (157) | 1.5 | 14 | 0.1 | 77 | 100 | H^\cdot abstraction |
| Trifluoromethyl iodide (196) | — | 10 | — | — | — | No reaction |
| Methyl iodide (142) | — | 16 | — | — | — | No reaction |
| Ethyl iodide (156) | 0.05 | 16 | 0.003 | 203 | 100 | I^\cdot abstraction |
| Isopropyl iodide (170) | 0.68 | 15 | 0.04 | 203 | 100 | I^\cdot abstraction |
| Allyl iodide (168) | 3.3 | 15 | 0.2 | 203 | 100 | I^\cdot abstraction |
| <i>tert</i> -Butyl iodide (184) | 3.8 | 16 | 0.2 | 203 | 100 | I^\cdot abstraction |

^a k_{exp} is given in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b k_{coll} is the collision rate given in units of $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Table 2. Reactions of ionized ethyl methyl sulfide ($IE = 8.5$ eV) with various neutral reagents

| Neutral reagent (MW) | IE^a (eV) | k_{exp}^b | k_{coll}^c | k_{exp}/k_{coll} | Product (m/z) | Branching ratio (%) | Reaction |
|--------------------------|-------------|-------------|--------------|--------------------|-------------------|---------------------|---|
| Dimethyl disulfide (94) | 8.0 | 11 | 18 | 0.6 | 94 | 100 | Charge exchange |
| Cyclohexa-1,4-diene (80) | 8.8 | 8.1 | 12 | 0.7 | 77 | 100 | H [•] abstraction |
| Benzeneselenol (157) | ≤ 7.7 | 11 | 15 | 0.7 | 77 | 30 | H [•] abstraction |
| | | | | | 157 ^d | 70 | Charge exchange |
| Allyl iodide (168) | 9.3 | 9.8 | 15 | 0.7 | 117 | 70 | CH ₂ =CHCH ₂ [•] abstraction |
| | | | | | 203 | 30 | I [•] abstraction |

^a All ionization energies are taken from Ref. 26 except for the ionization energy of dimethyl disulfide which was measured in our laboratory (Ref 27).

^b k_{exp} is given in units of 10^{-10} cm³ molecule⁻¹ s⁻¹.

^c k_{coll} is the collision rate constant given in units of 10^{-10} cm³ molecule⁻¹ s⁻¹.

^d Selenium isotope pattern was observed.

Table 3. Calculated absolute energies (MP2/6-31G*/6-31G* + ZPVE) and experimental heats of formation for several species of interest

| Molecule/ion | Absolute energy (hartree) | Experimental ^a ΔH_f (kJ mol ⁻¹) |
|--|---------------------------|--|
| (CH ₃) ₂ S ⁺ —CH ₂ [•] | -515.86153 | — |
| (CH ₃) ₃ S ⁺ | -516.51255 | 615 ^b |
| CH ₃ CH ₂ SCH ₃ ^{•+} | -515.88627 | 766 |
| CH ₄ | -40.28944 | -74 |
| CH ₃ [•] | -39.64079 | 146 |
| CH ₃ OH ₂ ⁺ | -115.58256 | 569 |
| [•] CH ₂ OH ₂ ⁺ | -114.92357 | 816 |

^a Ref. 26.

^b Determined in a flowing afterglow apparatus by a CAD threshold measurement (Ref. 28a) for the dissociation of (CH₃)₃S⁺ to CH₃[•] and (CH₃)₂S⁺ (Ref. 28b).

methyl sulfide, in addition to the C—H bond dissociation energy in (CH₃)₃S⁺. The optimized geometries of (CH₃)₂S⁺—CH₂[•] and (CH₃)₃S⁺ are shown in Fig. 3.

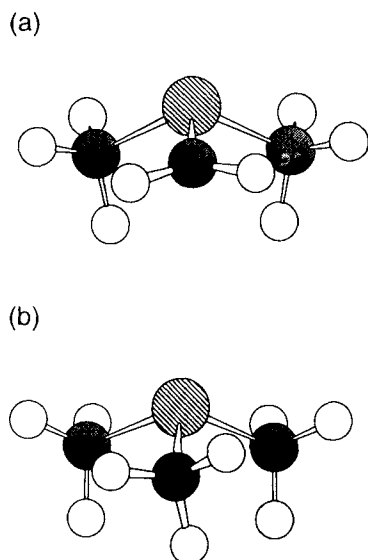
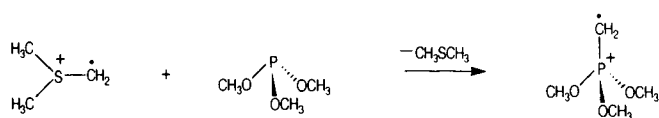


Figure 3. Optimized structures of (a) the methylenedimethylsulfonium ion (UHF/6-31G*) and (b) the trimethylsulfonium ion (HF/6-31G*).

DISCUSSION

The initial characterization of the methylenedimethylsulfonium ion relied on the reaction used to generate the ion and on its reactivity with dimethyl disulfide.⁶ The observation of abstraction of [•]SCH₃ as the only reaction with dimethyl disulfide suggested that the ion had a distonic structure. A later report distinguished the new ion from its conventional isomer, ionized ethyl methyl sulfide.¹⁴ On collision-activated dissociation, the distonic ion undergoes a minor loss of CH₂, which is not observed for ionized ethyl methyl sulfide. This result shows that the ion population is at least partially distinct from ionized ethyl methyl sulfide. However, these studies do not conclusively demonstrate that all of the ions of m/z 76 have the proposed α -distonic structure, i.e. a partial rearrangement cannot be ruled out. This possibility was examined by allowing the conventional ion to react with dimethyl disulfide. Very facile charge exchange was observed (Table 2, m/z 123). Since no charge exchange occurs on reaction of the distonic ion with dimethyl disulfide,⁶ none of the conventional isomer can be present in this ion population.

Transfer of the radical chain attached to a heteroatom is occasionally observed for distonic ions.^{2,3} If the new ion indeed had a CH₂ group attached to a sulfur atom, transfer of CH₂^{•+} might take place when the ion is allowed to react with strong nucleophiles. Various neutral molecules expected to be able to abstract CH₂^{•+} from the ion were examined. Ketones abstract CH₂^{•+} from various α -distonic ions, such as (CH₃)₂C⁺—OCH₂[•].¹³ However, the new ion was found to be unreactive toward cyclohexanone. A stronger base, triethylamine, reacts with the ion by an unexpected hydrogen atom transfer (Table 1). Trimethyl phosphite, a strong base (the proton affinity (PA) of trimethyl phosphite is 923 kJ mol⁻¹)²⁶ but a softer nucleophile than cyclohexanone and triethylamine, showed the expected reaction. This molecule rapidly abstracts ionized methylene from (CH₃)₂S⁺—CH₂[•], producing an ion which presumably has the structure (CH₃O)₃P⁺—CH₂[•] (Scheme 2). The observation of complete and exclusive methylene transfer (Fig. 4) conclusively demonstrates that all the reactant ions have the proposed α -distonic structure.



Scheme 2

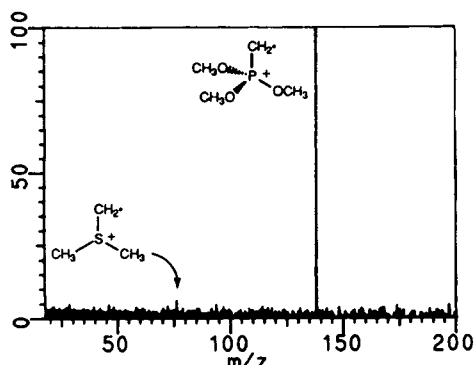


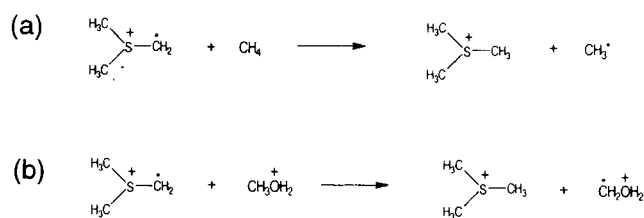
Figure 4. Reaction of the methylenedimethylsulfonium ion (m/z 76) with trimethyl phosphite resulting in exclusive transfer of CH_2^+ to give a product ion of m/z 138 assumed to have the structure $(\text{CH}_3\text{O})_3\text{P}^+-\text{CH}_2$.

Thermodynamic stability of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$

Simple sulfur-containing distonic ions are predicted to be less stable than their conventional counterparts.¹ Apart from $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$, the only other gaseous sulfur-containing distonic ion reported is the α -distonic ion $^-\text{CH}_2\text{SH}_2^+$ (formed by dissociation of the molecular ion of 2-mercaptoethanol).²⁹ On the basis of appearance energy measurements, the ion $^-\text{CH}_2\text{SH}_2^+$ has been estimated to be 28 kJ mol^{-1} higher in energy than its conventional counterpart, CH_3SH^+ .^{29c} *Ab initio* molecular orbital calculations at the MP3/6-31G**//4-31G level of theory place the latter ion 76 kJ mol^{-1} lower in energy than the distonic ion.³⁰

The currently accepted heat of formation for the ion $\text{CH}_3\text{CH}_2\text{SCH}_3^+$ is 764 kJ mol^{-1} .²⁶ If the stability difference between this ion and the distonic methylenedimethylsulfonium ion is similar to the difference for the lower homologs, $\text{H}_2\text{S}^+-\text{CH}_2$ and CH_3SH^+ ($28\text{--}76 \text{ kJ mol}^{-1}$), then the heat of formation of the methylenedimethylsulfonium ion is estimated to be $792\text{--}840 \text{ kJ mol}^{-1}$. This estimate is in agreement with the observation that reaction of neutral ketene with $\text{CH}_3\text{SCH}_3^+$ yields $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$ [Scheme 1(c)]:¹³ for this reaction to be exothermic, the heat of formation of $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$ must be less than 864 kJ mol^{-1} .

Ab initio molecular orbital calculations at the MP2/6-31G**//6-31G* + ZPVE level of theory were carried out to examine further the relative stabilities of the conventional ion $\text{CH}_3\text{CH}_2\text{SCH}_3^+$ and the methylenedimethylsulfonium ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$. The calculated enthalpy difference between the two ions was found to be 65 kJ mol^{-1} (Table 3). In order to obtain a more accurate estimate, isodesmic reactions were used to determine computationally the homolytic C—H bond dissociation energy in $(\text{CH}_3)_3\text{S}^+$ relative to that in CH_4 [Scheme 3(a)] and in CH_3OH_2^+ [Scheme 3(b)]. Using the calculated energies shown in Table 3, the



Scheme 3

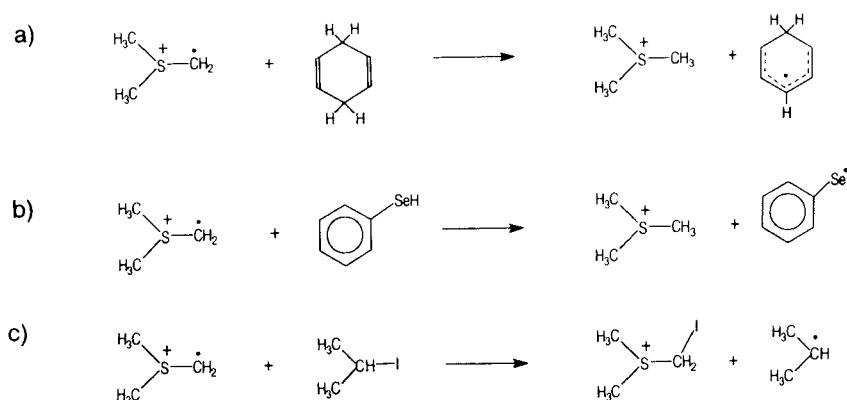
C—H bond in $(\text{CH}_3)_3\text{S}^+$ is estimated to be 6 kJ mol^{-1} stronger than the C—H bond in CH_4 (438 kJ mol^{-1})³¹ and 21 kJ mol^{-1} weaker than the C—H bond in CH_3OH_2^+ (466 kJ mol^{-1}).²⁶ Both of these values yield 444 kJ mol^{-1} as the homolytic C—H bond dissociation energy for $(\text{CH}_3)_3\text{S}^+$. This value is 57 kJ mol^{-1} higher than the C—H bond dissociation energy of CH_3SH (387 kJ mol^{-1}),³² a difference which is in excellent agreement with recent estimates for the relative homolytic C—H bond dissociation energies of neutral molecules and their protonated forms.³³ For example, that of CH_3OH is 393 kJ mol^{-1} ³⁴ and that of CH_3OH_2^+ is 456 kJ mol^{-1} , a difference of 63 kJ mol^{-1} .³³

The C—H bond energy calculated for $(\text{CH}_3)_3\text{S}^+$ yields our best estimate, 841 kJ mol^{-1} , for the heat of formation of the methylenedimethylsulfonium ion. This value is 75 kJ mol^{-1} above the enthalpy of the conventional isomer (within the range proposed above: $28\text{--}76 \text{ kJ mol}^{-1}$). It should be noted that although this distonic ion is significantly less stable than ionized ethyl methyl sulfide, it does not isomerize to the conventional structure. In sharp contrast, our preliminary investigation of the reactivity of $\text{H}_2\text{S}^+-\text{CH}_2$ shows that this ion undergoes facile rearrangement to CH_3SH^+ within the collision complex with various neutral molecules.

The optimized geometry of the ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$ and the even-electron analog $(\text{CH}_3)_3\text{S}^+$ are shown in Fig. 3. Removal of a hydrogen atom from $(\text{CH}_3)_3\text{S}^+$ results in a slight shortening of the S—C bond (from 1.80 to 1.75 \AA). The methylene group in the distonic ion is nearly planar, and does not have high barriers for rotation. For all the three ions, $\text{CH}_3\text{CH}_2\text{SCH}_3^+$, $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$, and $(\text{CH}_3)_3\text{S}^+$, the majority of the charge density resides on the sulfur atom (approximately $+0.7$). For the distonic ion, most of the odd-spin density resides on the methylene carbon ($1.3e$). Hence, the methylenedimethylsulfonium ion is truly a distonic ion: the charge site and the odd-spin site are located on different atoms in this ion. The chemical properties of the ion reflect this description.

Reactions with hydrogen atom donors

In solution, the measurement of rate constants for free-radical reactions can be accomplished by using a unimolecular radical clock,³⁵ or by trapping the radical intermediates for example by a fast hydrogen atom transfer reaction.³⁶ In order to probe the radical type properties of the ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2$, it was allowed to react with several hydrogen atom donors used for radical trapping in solution: cyclohexa-1,4-diene, thio-phenol and benzeneselenol.



The ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ undergoes the expected hydrogen atom abstraction reaction when allowed to react with cyclohexa-1,4-diene [Tables 1 and 2; Scheme 4(a)]. However, two other minor product ions are also generated (m/z 94 and 141; Table 1). These product ions arise from the transfer of a CH_2^+ group to cyclohexa-1,4-diene and by loss of a methyl radical from the adduct of the ion and cyclohexa-1,4-diene, respectively. The mechanisms of these reactions will be discussed in detail in another paper.^{28b} The conventional radical cation, *ionized ethyl methyl sulfide*, also abstracts a hydrogen atom from cyclohexa-1,4-diene. This reaction, however, is significantly faster than that of the distonic ion, indicating a different mechanism for the two reactions. It should be noted that the distonic ion was earlier reported to be unreactive toward cyclohexa-1,4-diene.¹⁴

The ion $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ reacts with thiophenol by abstraction of a hydrogen atom. This reaction is very slow (1% efficiency), the reaction rate being about one sixth of the H^\cdot -abstraction rate measured for cyclohexa-1,4-diene (6% H^\cdot -abstraction efficiency). Hence, this gaseous distonic ion shows a different relative efficiency for hydrogen atom abstraction from thiophenol and cyclohexa-1,4-diene than what has been observed in solution for neutral radicals. In general, thiophenol is a better hydrogen atom donor than cyclohexa-1,4-diene,³⁶ e.g., the cyclopropyl radical abstracts a hydrogen atom 500 times as fast from thiophenol as from cyclohexa-1,4-diene.³⁷

Benzeneselenol is the fastest pseudo-first-order radical trapping agent calibrated to date in solution.³⁸ This reagent reacts with primary alkyl radicals about 20 times faster than thiophenol.³⁸ Benzeneselenol was also found to be the most efficient hydrogen atom donor in

the experiments discussed here. This reagent transfers a hydrogen atom to $(\text{CH}_3)_2\text{S}^+-\text{CH}_2^\cdot$ at approximately 10% of the collision rate [Scheme 4(b); Table 1]: almost twice as fast as cyclohexa-1,4-diene and ten times as fast as thiophenol. Benzeneselenol reacts differently with ionized ethyl methyl sulfide than with the distonic ion in that reaction with the conventional radical cation leads to predominant charge exchange.

Table 4 shows the homolytic X—H (X = C, S, Se) bond dissociation energies of the three hydrogen atom donors studied. The Se—H bond strength in benzeneselenol has not been determined experimentally; therefore, the bond enthalpy of 280 kJ mol^{-1} given in Table 4 is an estimate (the authors of Ref. 38b assumed that the bond dissociation energy (BDE) difference between phenol and thiophenol was equal to the BDE difference between thiophenol and benzeneselenol). Experimental support for a low bond energy is obtained from the finding that benzeneselenol transfers a hydrogen atom to ionized aniline in the FT-ICR system, i.e. the reaction is exothermic. Hence, the Se—H bond strength must be less than the hydrogen atom affinity of ionized aniline (305 kJ mol^{-1}).²⁶

The efficiency of hydrogen atom abstraction by the methylenedimethylsulfonium ion correlates with the homolytic X—H (X = C, S, Se) bond dissociation energy of the hydrogen atom donor (Table 4), and therefore with the exothermicity of the reaction. Further, all the hydrogen atom abstraction reactions studied occur at a rate significantly less than the collision rate, in spite of the fact that these reactions are highly exothermic (Table 4). For example, abstraction of a hydrogen atom from thiophenol by the methylenedimethylsulfonium ion is estimated to be exothermic

Table 4. Homolytic bond dissociation energies for various hydrogen atom donors, together with the observed efficiency and ΔH for H^\cdot abstraction

| Neutral reagent | X—H (X = C, S, Se) homolytic bond dissociation energy (kJ mol^{-1}) | Efficiency of H^\cdot abstraction | ΔH_{rxn} (kJ mol^{-1}) |
|---------------------|--|--|--|
| Thiophenol | 349 ^a | 0.01 | -95 |
| Cyclohexa-1,4-diene | 305 ^b | 0.06 | -139 |
| Benzeneselenol | 280 ^c | 0.10 | -164 |

^a Ref. 34.

^b Assumed to be the same as in cyclohexa-1,3-diene; Refs 26 and 34.

^c Ref. 38. See comment in text.

by 95 kJ mol⁻¹ but it only occurs for one collision out of 100. Both of these findings suggest that a substantial energy barrier on the reaction coordinate is the main factor controlling the reaction rate.

Substantial activation energies are known to be associated with hydrogen atom abstraction by many neutral alkyl radicals, e.g. the abstraction of a hydrogen atom from methane by the methyl radical has an energy barrier of 63 kJ mol⁻¹.³⁹ Hence, the observation of slow reaction rates for the distonic ion, as compared to cationic reactions (e.g. hydrogen atom abstraction by ionized ethyl methyl sulfide), are in agreement with a radical mechanism. It should be noted that partial charge transfer in the transition state does not seem to play an important role. The relative ease of charge transfer³⁹ does not correlate with the observed trend in the reaction rates for the different hydrogen atom donors (the ionization energies²⁶ are 8.3 eV for thiophenol, 8.8 eV for cyclohexa-1,4-diene and 7.7 eV for benzeneselenol). The observations made for the distonic ion (CH₃)₂S⁺—CH₂[•] are best explained on the basis of a simple radical abstraction mechanism.

Reactions with alkyl iodides

Free-radical substitution reactions involving molecular iodine and alkyl iodides are well characterized both in solution and in the gas phase.⁴⁰ In order to examine further whether the methylenedimethylsulfonium ion exhibits reactivity similar to that of free alkyl radicals, the ion was allowed to react with a series of alkyl iodides. The ion (CH₃)₂S⁺—CH₂[•] is unreactive toward methyl iodide and trifluoromethyl iodide. Ethyl iodide, isopropyl iodide [Scheme 4(c)], *tert*-butyl iodide and allyl iodide slowly transfer an iodine atom to the ion. Again, ionized ethyl methyl sulfide reacts differently: the reaction with allyl iodide leads to predominant CH₂=CHCH₂[•] abstraction (Table 2).

The homolytic bond strengths of alkyl iodides are, at best, known to within 4 kJ mol⁻¹.^{26,31} However, the bond strengths for the series of methylated alkyl iodides are expected to follow the trend methyl iodide > ethyl iodide > isopropyl iodide > *tert*-butyl iodide (Table 5). The efficiency of I[•] abstraction by the distonic ion increases in the same order, and allyl iodide which contains the weakest carbon–iodine bond of the compounds studied transfers an iodine atom to (CH₃)₂S⁺—CH₂[•] at the highest efficiency.

Table 5. Homolytic bond dissociation energies for alkyl iodides and the observed efficiencies for I[•] abstraction

| Alkyl iodide | C—I homolytic bond dissociation energy ^a (kJ mol ⁻¹) | Efficiency of I [•] abstraction |
|---------------------------|---|--|
| Methyl iodide | 237 | — |
| Ethyl iodide | 234 | 0.003 |
| Isopropyl iodide | 235 ^{a, b} | 0.044 |
| <i>tert</i> -Butyl iodide | 227 | 0.23 |
| Allyl iodide | 168 | 0.26 |

^a Refs 26 and 31.

^b Based on $\Delta H_f(i-C_3H_7I) = -39.3$ kJ mol⁻¹; Ref. 41.

The rate of iodine atom abstraction by neutral radicals is governed by the activation energy, which in turn is predominantly, but not exclusively, determined by the exothermicity of the reaction.^{42–44} The observation of a dependence between the iodine atom abstraction efficiency by (CH₃)₂S⁺—CH₂[•] and the homolytic C—I bond dissociation energy of the alkyl iodide supports a simple radical abstraction mechanism for these reactions. The low efficiency of all the reactions suggests a significant energy barrier on the reaction coordinate [see Fig. 5(a)], just as was the case for the hydrogen atom abstraction reactions. However, the very large increase in the reaction efficiency on going from ethyl iodide to *tert*-butyl iodide suggests that other factors, in addition to the increase in reaction exothermicity (which is very small), must be considered. This proposal is further supported by the observed inability of trifluoromethyl iodide to transfer iodine to the ion.

Although the C—I bond strength in trifluoromethyl iodide is roughly the same as that in ethyl iodide, trifluoromethyl iodide does not react with (CH₃)₂S⁺—CH₂[•]. This observation may be partially explained by unfavorable polar effects in the transition state for the fluorinated iodide. Trifluoromethyl iodide is less reactive toward electrophilic radicals (but more reactive toward nucleophilic radicals such as the methyl radical) than other alkyl iodides with similar C—I bond strengths due to increased repulsive polar effects in the transition state.⁴⁴ The methylenedimethylsulfonium ion can be viewed as an electrophilic radical due to the presence of the electron-withdrawing sulfonium substituent at the α -position. Upon iodine atom abstraction from trifluoromethyl iodide, there is likely to be repulsion between the positive charge in the ion and the partial positive charge on the carbon of the trifluoromethyl group, resulting in an increased barrier as compared to that of the alkyl iodide reactions.

Further, the lack of reactivity of trifluoromethyl iodide toward the methylenedimethylsulfonium ion is partially (if not entirely) explained by the fact that trifluoromethyl iodide has a very small dipole moment (0.48 D)⁴⁵ and is therefore a poor 'solvent' for the charged radical. The potential energy well corresponding to the collision complex of trifluoromethyl iodide is very shallow: the well depth is estimated to be only 25 kJ mol⁻¹ whereas those estimated for the alkyl iodides are around 40 kJ mol⁻¹ [Fig. 5(b)].⁴⁶ Hence, whereas a collision complex of the distonic ion with an alkyl iodide has about 40 kJ mol⁻¹ excess energy to overcome barriers on the reaction coordinate, the collision complex of trifluoromethyl iodide has only 25 kJ mol⁻¹. The barrier associated with iodine atom abstraction from an alkyl iodide by the distonic ion is likely to be close to 40 kJ mol⁻¹ (the barrier must be comparable to the ion–molecule attraction energy in order to have such a strong effect on the reaction efficiency as is observed) [see Fig. 5(a)]. Assuming that the energy barrier for the fluorinated iodide is at least as high (although it is likely to be greater), this barrier is almost certainly above the energy of the reactants [Fig. 5(b)]. Since endothermic reactions are not observed in the experiments discussed here, iodine abstraction from trifluoromethyl iodide is concluded to be inaccessible for the distonic ion. Differences in the well depths and

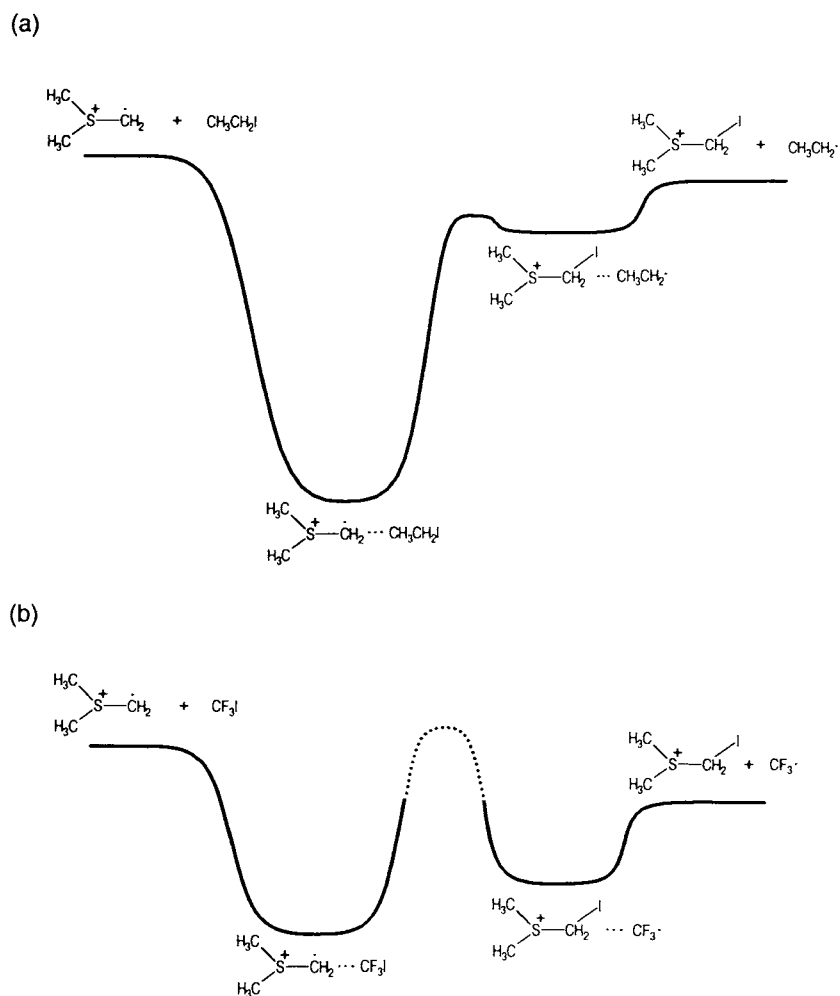


Figure 5. Potential energy diagram for the reaction of the methylenedimethylsulfonium ion with (a) ethyl iodide and (b) trifluoromethyl iodide. The well depths were estimated according to Ref. 44.

lifetimes of the ion-molecule collision complexes, together with a decrease in the relatively high transition-state energy, probably explains the large rate increase for alkyl iodides when the alkyl group becomes larger.

CONCLUSIONS

The ion $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ has been characterized by using ion-molecule reactions and *ab initio* molecular orbital calculations. $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ is estimated to be 75 kJ mol^{-1} higher in energy than ionized ethyl methyl sulfide. However, the distonic ion is stable toward isomerization to the conventional structure, as demonstrated by the distinctly different reactivity observed for the two ions. Most importantly, the observation of an exclusive and complete CH_2^+ transfer to trimethyl phosphite shows that all the ions $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ have the proposed α -distonic structure.

Ab initio molecular orbital calculations show that $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ is a true distonic ion, with the charge site at the sulfur atom while the odd-spin density is localized on the CH_2 group. The chemical properties of the ion reflect this description: most of its reactions

involve a homolytic bond cleavage in the neutral molecule and result in abstraction of an atom or a radical by the ion. These reactions are significantly slower than the analogous reactions of the conventional radical cation, indicating a different mechanism for the two ions. The efficiency of atom abstraction by $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ correlates with the homolytic bond energy of the breaking bond. All these findings support a simple radical abstraction mechanism for atom abstraction by $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$. On the basis of its reactivity, this distonic ion is best described as an electrophilic radical with an inert charge site. In this sense, $(\text{CH}_3)_2\text{S}^+-\dot{\text{C}}\text{H}_2$ differs remarkably from other distonic ions, such as $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$, which undergo reactions initiated by covalent bond formation at the charge site.

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