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Reactions of the Charged Radical $(CH_3)_2S^+-CH_2^{\bullet}$ with Cyclic Alkenes

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Abstract: The gas-phase reactivity of the charged radical $(CH_3)_2S^+-CH_2^{\bullet}$ (a distonic ion) resembles closely the reactivity of neutral alkyl radicals toward cyclic alkenes. $(CH_3)_2S^+-CH_2^{\bullet}$ adds to alkenes or abstracts a hydrogen atom from the alkenes to form the trimethylsulfonium ion $(CH_3)_3S^+$. The lowest-energy conformer of $(CH_3)_2S^+-CH_2^{\bullet}$ is calculated to have a hydrogen atom affinity of 443 kJ mol^{-1} (UMP2/6-31G*//UHF/6-31G* + ZPVE). Hence, the observed hydrogen atom abstraction reactions are predicted to be highly exothermic (up to 138 kJ mol^{-1}). However, these reactions occur at a low efficiency, suggesting the presence of a relatively high barrier on the reaction coordinate. Therefore, hydrogen atom abstraction by the charged radical must occur through a different mechanism than the reaction for the isomeric radical cation $CH_3CH_2SCH_3^{\bullet+}$ which efficiently abstracts a hydrogen atom from the alkenes. The heat of formation of $(CH_3)_3S^+$ is determined to be 615 ± 15 kJ mol^{-1} by measuring the threshold energy for the dissocation of $(CH_3)_3S^+$ to $(CH_3)_2S^{\bullet+}$ and $CH_3^{\bullet}$ in a flowing afterglow−triple quadrupole apparatus. This value, together with the hydrogen atom affinity calculated for $(CH_3)_2S^+-CH_2^{\bullet}$, yields a heat of formation of 840 kJ mol^{-1} for the lowest-energy conformer of $(CH_3)_2S^+-CH_2^{\bullet}$. Hence, the distonic ion is about 74 kJ mol^{-1} higher in energy than the radical cation $CH_3CH_2SCH_3^{\bullet+}$. However, the different chemical properties of these two isomeric ions demonstrate that they are stable toward isomerization.

Introduction

Distonic radical cations, radicals with a spatially separated charge site,[1a] have been of considerable interest during recent years.[1,2] These species show reactivity quite different from that of conventional radical cations.[3] For example, many distonic ions undergo radical-type atom abstraction reactions that are not observed for related conventional radical cations (*e.g.*, halogen abstraction).[3,4] Distonic ions that react preferentially at the odd-spin site are particularly interesting because these ions may offer a means to examine gaseous free radical chemistry by using mass spectrometry.[4]

The methylenedimethylsulfonium ion, $(CH_3)_2S^+-CH_2^{\bullet}$, is one of the few distonic ions known to have a coordinately saturated and relatively unreactive charge site.[5−7] Indeed, most of the reactions reported for this ion involve abstraction of an odd-electron moiety.[5−7] For example, $(CH_3)_2S^+-CH_2^{\bullet}$ reacts with dimethyl disulfide by exclusive thiomethyl abstraction and with alkyl iodides by iodine atom abstraction.[5] In this sense, the ion is best described as a reactive radical with an inert charge site.

Besides atom abstraction reactions, addition to carbon−carbon double bonds is commonly observed for neutral alkyl radicals. Addition reactions have not been systematically examined for any distonic ion. We report here a comparison of the intrinsic (gas-phase) reactivity of the ion $(CH_3)_2S^+-CH_2^{\bullet}$ and its conventional isomer $CH_3CH_2SCH_3^{\bullet+}$ toward cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene. The reactions of $(CH_3)_2S^+-CH_2^{\bullet}$ proceed via hydrogen atom abstraction and radical addition to the alkene. This reactivity is quite different from that of the conventional radical cation.

Experimental Section

All reagents were obtained from commercial suppliers and used as received or purified by standard methods. The purity of each compound was checked by gas chromatography and by mass spectrometry. The 1,4-cyclohexadiene was found to be contaminated with minor amounts of 1,3-cyclohexadiene and was purified by preparative GC using a 12 ft × 4 mm i.d. column packed with 10% OV-101 on 60−80 mesh Chromosorb W-NAW. 1-Methyl-1,3-cyclohexadiene was obtained from Bedoukian Research, Inc., purified as described above, and checked for purity by using gas chromatography, mass spectrometry, and ^1H NMR.

Ion−molecule reactions were examined using a dual-cell Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometer (Extrel FTMS Model 2001) which has been described in detail earlier.[8] Samples were introduced into the FT-ICR by using two Extrel-manufactured single batch inlet systems equipped with variable leak valves or by using a Varian Model 951-5106 leak valve. Ethyl methyl sulfide was ionized by electron impact (20−30 eV electron energy, 4−8 μA emission current, 40−100 ms beam time). The methylenedimethylsulfonium ion was formed by reaction of dimethyl sulfide with $^{\bullet}CH_2OCH_2^+$ which in turn was formed by electron ionization of ethylene oxide under the conditions described above; the total pressure of ethylene oxide and dimethyl sulfide was *ca.* 4×10^{-5} Pa. The ions were generated in one side of the dual cell and transferred into the other side for reactivity studies. After transfer, the ions were cooled[8] through numerous collisions with argon added using a pulsed valve assembly. Ion isolation was performed by applying a series of single frequency voltage pulses and stored waveform inverse Fourier transform waveforms[9] to the excitation plates of the cell (by using an

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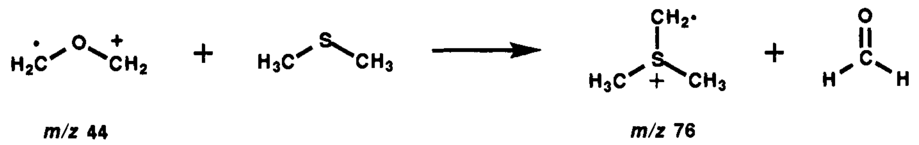
Scheme 1



Extrel FTMS SWIFT module). Care was taken to avoid translational excitation of the ion during the isolation procedure. The isolated ions were allowed to react with the desired neutral reagent (typically at a nominal pressure of 1.3×10^{-5}–5.3×10^{-5} Pa) for a variable period of time (500 ms–20 s). Ions were excited for detection by using an excitation frequency sweep ("chirp") of 124 $V_{p\text{-}p}$ amplitude, 2.7 MHz bandwidth, and either 2.2 or 3.0 kHz/μs sweep rate or by using a stored inverse Fourier-transform[9] waveform. 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. Each spectrum is an average of at least 32 acquisitions.

The branching ratios of the different reaction channels were derived from the relative abundances of the product ions measured at short reaction times. The experimental rate constant, k_{exp}, was derived from the slope of a plot of the logarithm of the reactant ion's relative abundance *vs* time. The collision rate constant, k_{coll}, was calculated using a theoretical model.[10] The total reaction efficiency is given by k_{exp}/k_{coll}. For rate measurements, the ion gauges were calibrated for the sensitivity[11] of the neutral reagent and for the pressure gradient between the dual cell and the ion gauge. A correction factor for the pressure gradient was obtained by measuring the rate constant for the protonation of 1,4-cyclohexadiene with H_3S^+. This reaction was assumed to proceed at the collision rate, an assumption that is usually valid for highly exothermic proton transfer reactions.[12,13] Precision of the rate measurements for the ion–molecule reactions is better than ±10% and the accuracy is estimated to be better than ±50%.

The enthalpy change for the dissociation of $(CH_3)_3S^+$ to $(CH_3)_2S^{\bullet+}$ and $CH_3^\bullet$ was measured in a flowing afterglow–triple quadrupole apparatus that has been previously described.[14] The trimethylsulfonium ion was prepared in the flow tube of the instrument by reaction of $(CH_3)_2F^+$ (generated by self-chemical ionization of CH_3F) with $(CH_3)_2S$, thermalized to room temperature by collisions with the helium carrier gas, and extracted into the low pressure region which contains the triple quadrupole mass spectrometer. The ion $(CH_3)_3S^+$ was mass selected with the first quadrupole and injected into the second radiofrequency-only quadrupole that functions as a gas-tight collision chamber. Argon was used as the collision gas at a pressure below 6.7×10^{-3} Pa (single collision conditions). The kinetic energy of the ion is determined by the offset voltage (relative to ground) of the middle quadrupole; this offset was scanned from 0 to 30 V. The reactant and product ions were analyzed with the third quadrupole and detected with an electron multiplier operated in the pulse-counting mode.

The analysis procedures which were used to treat the data obtained from the CAD threshold energy measurements have been described previously.[15] A plot of the normalized product ion yield versus the center-of-mass collision energy yields a curve from which the activation energy for the dissociation can be derived. The steeply rising portion of the curve was iteratively fit with a model threshold law that takes into account certain broadening functions and the kinetic shift due to slow (on the experimental time scale) unimolecular decomposition of the reactant ion.[15c,16] The threshold energy derived in this manner corresponds to 0 K dissociation energy. The enthalpy change of the dissociation at 298 K was obtained by adding the difference in the integrated heat capacities of the reactant and product ions as well as a *PV* work term ($RT = 2.5$ kJ mol^{-1} at 298 K).

Ab initio molecular orbital calculations were carried out using the Gaussian 90 (revision F) series of programs.[17] The geometries were fully optimized using the UHF/6-31G* basis set.[18] One geometry (Figure 2a) was checked at the UMP2/6-31G* level and found to be the same as at the UHF/6-31G* level. Zero-point vibrational energies (ZPVE) were calculated from the UHF/6-31G* vibrational frequencies and scaled by a factor of 0.9 to account for the systematic overestimation of the vibrational frequencies by Hartree–Fock calculations.[19] Single-point calculations were carried out at the UMP2/6-31G*//UHF/6-31G* + ZPVE level of theory.[20] The force constant matrices for the stationary points were checked to have the correct number of negative eigenvalues (zero for the equilibrium structures shown in Figure 2, a and b). The spin contamination, $\langle S^2 \rangle$, was within acceptable range (0.764–0.765) from the value of 0.75 for the pure spin state.

Results and Discussion

The ion $(CH_3)_2S^+{-}CH_2^\bullet$ was generated in one side of the dual cell of the Fourier-transform ion cyclotron resonance instrument (FT-ICR) by reaction of $^\bullet CH_2OCH_2^+$ with dimethyl sulfide (Scheme 1; Figure 1a–c), transferred into the other side, collisionally cooled, isolated (Figure 1d), and allowed to react with an alkene (Figure 1e). The primary reaction products and reaction rate constants, together with the calculated ion–molecule collision rate constants[10] and reaction efficiencies (k_{exp}/k_{coll}), are given in Table 1 for the alkenes studied. The corresponding data for $CH_3CH_2SCH_3^{\bullet+}$ are given in Table 2.

Reaction with 1,4-Cyclohexadiene. The homolytic bond dissociation energy of the allylic C–H bonds in 1,4-cyclohexadiene is relatively low (305 kJ mol),[21] which allows the use of 1,4-cyclohexadiene to trap free radicals by hydrogen atom transfer.[22] As expected, hydrogen atom transfer also dominates the reaction of the charged radical $(CH_3)_2S^+{-}CH_2^\bullet$ with 1,4-cyclohexadiene (almost 60% of the product distribution arises from hydrogen atom transfer, *m/z* 77). This finding is in agreement with the results presented in a recent communication.[7] The product ion is likely to be the trimethylsulfonium ion, $(CH_3)_3S^+$. As expected for this structure, the ion is unreactive toward 1,4-cyclohexadiene.

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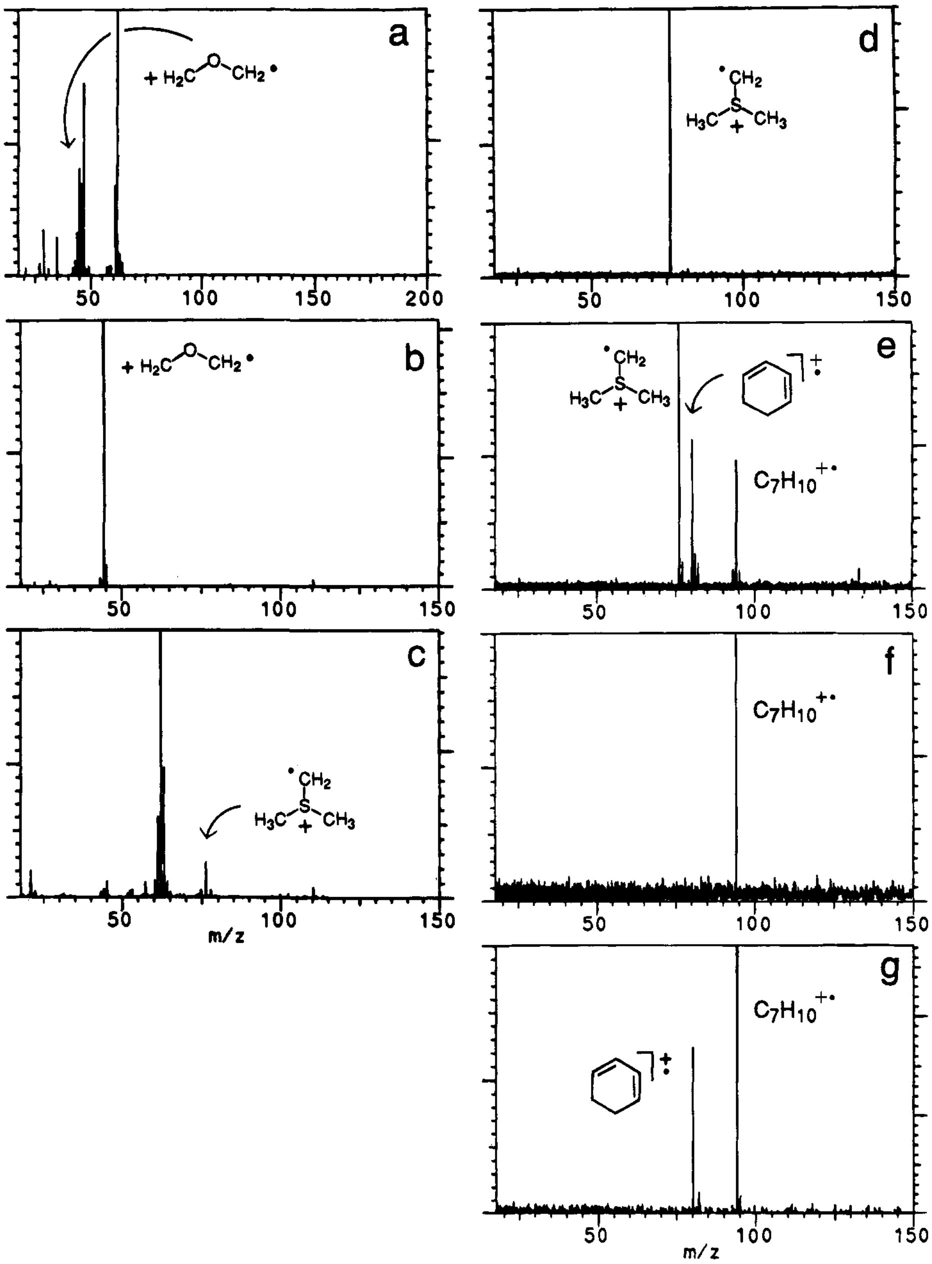


Figure 1. (a) Electron ionization of ethylene oxide and dimethyl sulfide. (b) Isolation of $^•CH_2OCH_2^+$ (*m/z* 44). (c) Reaction of $^•CH_2OCH_2^+$ with dimethyl sulfide. (d) Transfer of $(CH_3)_2S^+{-}CH_2^•$ (*m/z* 76) into the other cell followed by isolation. (e) Reaction of $(CH_3)_2S^+{-}CH_2^•$ with 1,3-cyclohexadiene. (f) Isolation of the major primary product ion $C_7H_{10}^+$ (*m/z* 94). (g) Reaction of the ion of *m/z* 94 with 1,3-cyclohexadiene.

Table 1. Reactions of $(CH_3)_2S^+{-}CH_2^•$ (*m/z* 76) with Various Cyclic Alkenes

neutral reagent (MW)	k_{exp}[a]	k_{coll}[b]	k_{exp}/k_{coll}	primary products (*m/z*)	branching ratios (%)	reaction
cyclohexene (82)	0.4	13	0.04	63	12	$(CH_3)_2SH^+$
				77	17	$H^•$ abstraction
				96	36	$CH_2^{•+}$ transfer
				143	35	adduct$-CH_3^•$
1,3-cyclohexadiene (80)	3.3	13	0.3	77	9	$H^•$ abstraction
				94	91[c]	$CH_2^{•+}$ transfer
1,4-cyclohexadiene (80)	1.1	12	0.1	77	56	$H^•$ abstraction
				94	24	$CH_2^{•+}$ transfer
				141	20	adduct$-CH_3^•$

[a] k_{exp} is given in units of $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. [b] k_{coll} is the collision rate given in units of $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. [c] Extrapolated to zero reaction time.

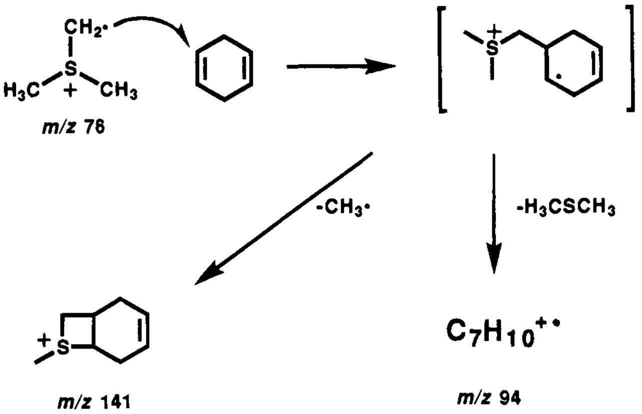
Besides trimethylsulfonium ion, two other primary product ions are also generated upon reaction of $(CH_3)_2S^+{-}CH_2^•$ with 1,4-cyclohexadiene: the ions of *m/z* 94 and 141 (Table 1; the three ions were demonstrated to be primary products by continuously ejecting each ion from the cell during the reaction time of different experiments: this had no effect on the other two product ions). The two product ions arising from reactions other than hydrogen atom abstraction are formed via addition of the radical site of $(CH_3)_2S^+{-}CH_2^•$ to the alkene. One of these product ions arises from the loss of a methyl radical from the initially formed adduct[7] and may have the bicyclic structure shown in Scheme 2 (*m/z* 141). The other product ion, a radical

Table 2. Reactions of Ionized Ethyl Methyl Sulfide (*m/z* 76) with Various Cyclic Alkenes

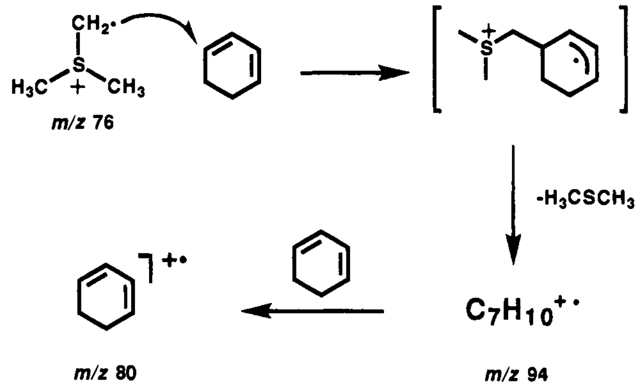
neutral reagent (MW)	k_{exp}[a]	k_{coll}[b]	k_{exp}/k_{coll}	primary products (*m/z*)	branching ratios (%)	reaction
cyclohexene (82)	5.8	13	0.4	77	100	H$^•$ abstraction
1,3-cyclohexadiene (80)	13	13	1.0	77	30	H$^•$ abstraction
				80	70	charge transfer
1,4-cyclohexadiene (80)	7.1	12	0.6	77	100	H$^•$ abstraction

[a] k_{exp} is given in units of $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. [b] k_{coll} is the collision rate constant given in units of $\times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.

Scheme 2



Scheme 3



cation $C_7H_{10}^{•+}$ (*m/z* 94), arises from the loss of CH_3SCH_3 from the initially generated adduct (Scheme 2). A direct displacement of CH_3SCH_3 by 1,4-cyclohexadiene in $(CH_3)_2S^+{-}CH_2^•$ is ruled out on the basis of the earlier finding[5] that this ion does not generally transfer $CH_2^{•+}$ to neutral molecules. Even such relatively strong nucleophiles as cyclohexanone and triethylamine, reagents that readily abstract $CH_2^{•+}$ from many distonic ions,[3-5] are unreactive toward $(CH_3)_2S^+{-}CH_2^•$. In fact, trimethyl phosphite is the only neutral reagent known to directly abstract $CH_2^{•+}$ from $(CH_3)_2S^+{-}CH_2^•$.[5]

It is interesting to note that the competing hydrogen atom abstraction and radical addition channels for the reaction of $(CH_3)_2S^+{-}CH_2^•$ with 1,4-cyclohexadiene have an almost equal probability (1.3:1.0). Similar behavior has been reported recently for the reaction of the OH radical with 1,4-cyclohexadiene in solution.[23a] In the gas phase at atmospheric pressure, however, addition seems to dominate.[23b,c] The branching ratio measured for the reaction of $(CH_3)_2S^+{-}CH_2^•$ with 1,3-cyclohexadiene (see below) is identical to that reported for the OH radical at atmospheric pressure in the gas phase.[23c]

In addition to the three product ions discussed above, $(CH_3)_2SH^+$ has been reported[7] to be formed upon reaction of $(CH_3)_2S^+{-}CH_2^•$ with 1,4-cyclohexadiene in a single-cell FT-ICR instrument. This product ion, however, was not detected in the dual-cell instrument wherein the reaction was carried out in the absence of dimethyl sulfide, the neutral precursor to $(CH_3)_2S^+{-}CH_2^•$. This finding suggests that $(CH_3)_2SH^+$ formed in the earlier study arises from a reaction involving neutral dimethyl sulfide rather than 1,4-cyclohexadiene.

Reaction with Cyclohexene. The charged radical $(CH_3)_2S^+{-}CH_2^•$ reacts with cyclohexene to yield analogous product ions as were obtained for 1,4-cyclohexadiene (a minor amount of $(CH_3)_2SH^+$ is also formed). However, the reaction efficiencies and the relative abundances of the products are quite different for the two alkenes. Hydrogen atom abstraction is much less favored (17% of the total product ions) for cyclohexene than for 1,4-cyclohexadiene (56%). Further, the H-atom abstraction efficiency (k_{exp}/k_{coll}) is only 0.007 for cyclohexene but almost an order of magnitude greater for 1,4-cyclohexadiene (0.06). The low efficiency of hydrogen atom abstraction relative to other reaction channels in the case of cyclohexene (as well as the low overall efficiency of the reaction) is likely due to the higher allylic C−H bond enthalpy of cyclohexene as compared to that of 1,4-cyclohexadiene (347 kJ mol^{-1} versus 305 kJ mol^{-1}).[21] An analogous trend in reactivity was reported earlier for the reaction of $(CH_3)_2S^+{-}CH_2^•$ with alkyl iodides: iodine atom abstraction efficiency decreases dramatically with an increasing homolytic C−I bond enthalpy.[5] These observations support a simple radical abstraction mechanism for the atom abstraction reactions of $(CH_3)_2S^+{-}CH_2^•$.

In contrast to the difference in the efficiency of hydrogen atom abstraction by $(CH_3)_2S^+{-}CH_2^•$ from cyclohexene and 1,4-cyclohexadiene, *radical addition* occurs at a similar efficiency for the two alkenes: 3% of the collisions with cyclohexene and 4% of the collisions with 1,4-cyclohexadiene lead to products that arise from reactions expected to follow addition of the charged radical to the alkene (Scheme 2). The branching ratios of these product ions are similar: the observed ratio of $CH_2^{•+}$ to $CH_3SCH_2^+$ transfer (adduct $-CH_3^•$) is 1.0:1.0 for cyclohexene and 1.2:1.0 for 1,4-cyclohexadiene. Indeed, addition is expected to be nearly equally exothermic for both alkenes, and the branching ratios of the following reactions might also be expected to be similar if they occur as shown in Scheme 2.

Reaction with 1,3-Cyclohexadiene. The homolytic bond dissociation energies of the allylic C−H bonds in 1,4- and 1,3-cyclohexadienes are comparable (the bond in 1,3-cyclohexadiene is about 2 kJ mol^{-1} stronger).[22,24] Since 1,4-cyclohexadiene readily transfers a hydrogen atom to $(CH_3)_2S^+{-}CH_2^•$, the same reaction was expected to take place for 1,3-cyclohexadiene. However, the reaction with 1,3-cyclohexadiene produces only a minor amount of the hydrogen atom transfer product (9%). The major reaction channel (about 90%) involves radical addition to the diene, followed by loss of CH_3SCH_3 to yield a hydrocarbon radical cation $C_7H_{10}^{•+}$ (*m/z* 94). The strong preference of $(CH_3)_2S^+{-}CH_2^•$ to add to this particular alkene is likely due to the fact that an allylic radical is generated (Scheme 3). Being less reactive than the localized radical formed from 1,4-cyclohexadiene and cyclohexene, the allylic

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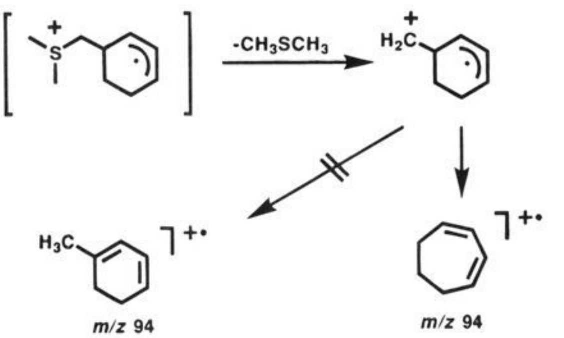
Scheme 4



radical does not attack the sulfur atom to replace a methyl radical but undergoes C−S bond cleavage to eliminate CH_3SCH_3.

The radical cation product $C_7H_{10}^{•+}$ reacts with 1,3-cyclohexadiene (ionization energy 8.3 eV[24]) by charge transfer to yield ionized 1,3-cyclohexadiene (*m/z* 80). This reaction sequence was verified by continuously ejecting the reactant ion out of the cell during the reaction time: the ejection resulted in the disappearance of the ionized 1,3-cyclohexadiene. In a separate experiment, the $C_7H_{10}^{•+}$ ion was isolated (Figure 1f) and allowed to react with neutral 1,3-cyclohexadiene: ionized 1,3-cyclohexadiene was the only product ion formed (Figure 1g).

The observation of facile charge transfer for the $C_7H_{10}^{•+}$ ion suggests that this radical cation is not a distonic ion.[3,4] However, elimination of CH_3SCH_3 from the initially formed adduct through a simple C−S bond cleavage would yield a distonic ion, a derivative of the ring-opened ionized cyclopropane (Scheme 4). If the reaction occurs through this mechanism, the product ion must subsequently isomerize to a conventional radical cation. Ring closure to yield ionized cyclopropane is ruled out since the thoroughly studied prototypical ion $^•CH_2CH_2CH_2^+$ (calculated at the MP2/6-31G*//UHF/6-31G* level of theory to lie 91 kJ mol^{-1} higher in energy than ionized cyclopropane[3]) does not isomerize to ionized cyclopropane but to ionized propene by a 1,2-hydride shift.[25] A 1,2-hydride shift in the distonic $C_7H_{10}^{•+}$ ion generated upon simple $CH_2^{•+}$ transfer to 1,3-cyclohexadiene would yield the very stable[24] ionized 1-methyl-1,3-cyclohexadiene (Scheme 4). However, this structure is ruled out on the basis of the observation that a reference ion generated by ionization of 1-methyl-1,3-cyclohexadiene is unreactive toward 1,3-cyclohexadiene. An alternative isomerization through ring enlargement might yield ionized 1,3-cycloheptadiene (Scheme 4). A reference ion with this structure was generated and indeed found to undergo facile charge exchange with 1,3-cyclohexadiene (the reaction[24] is exothermic by 0.1 eV). Hence, the long-lived $C_7H_{10}^{•+}$ ion generated upon reaction of $(CH_3)_2S^+-CH_2^•$ with 1,3-cyclohexadiene likely has the 1,3-cycloheptadiene structure.

The reactivity observed for the product ions arising from $CH_2^{•+}$ transfer to the other two alkenes, cyclohexene and 1,4-cyclohexadiene provides further support for the mechanism in Scheme 4. Charge exchange involving these alkenes and the $CH_2^{•+}$ transfer product formed from each alkene is estimated[24] to be slightly endothermic if the two ions have the expected cycloheptene and 1,4-cycloheptadiene structures. Indeed, the product ion (*m/z* 96) formed from cyclohexene, as well as authentic ionized cycloheptene, were found to be unreactive toward cyclohexene. The ion formed from 1,4-cyclohexadiene does not undergo charge exchange but hydrogen atom abstraction when allowed to react with 1,4-cyclohexadiene.

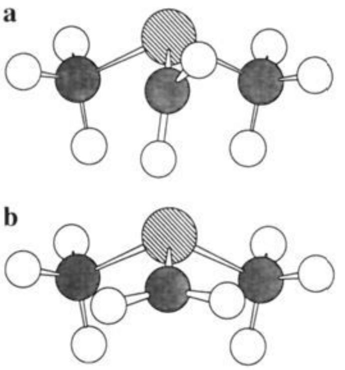


Figure 2. Two optimized geometries of $(CH_3)_2S^+-CH_2^•$ at the UHF/6-31G* level of theory.

Reactions of Ionized Ethyl Methyl Sulfide. The conventional radical cation $CH_3CH_2SCH_3^{•+}$ shows quite different reactivity than its distonic isomer. Ionized ethyl methyl sulfide (recombination energy 8.54 eV[24]) reacts with 1,3-cyclohexadiene (ionization energy 8.25 eV[24]) by facile electron transfer (exothermic by 28 kJ mol^{-1}), a reaction not observed for the distonic ion. Electron transfer from cyclohexene (ionization energy 8.9 eV) or 1,4-cyclohexadiene (ionization energy 8.8 eV) to ionized ethyl methyl sulfide is endothermic[24] and was not observed. Hydrogen atom abstraction (exothermic for all three alkenes[24]) is the only reaction observed for cyclohexene and 1,4-cyclohexadiene. Hydrogen atom abstraction accompanies the dominant charge exchange also for 1,3-cyclohexadiene, (Table 2).

The efficiency of hydrogen atom abstraction by ionized ethyl methyl sulfide approaches the collision rate, being significantly more efficient than H-abstraction by the distonic ion. This finding suggests that different mechanisms are operative upon hydrogen abstraction by the distonic ion and by the conventional ion. Based on the calculated homolytic C−H bond enthalpy of $(CH_3)_3S^+$ (443 kJ mol^{-1}; see below), hydrogen atom abstraction by $(CH_3)_2S^+-CH_2^•$ is exothermic by more than 100 kJ mol^{-1} for the alkenes studied. Hence, the slow rate of hydrogen atom abstraction by the distonic ion cannot arise from the lack of thermodynamic driving force but implies the presence of a relatively large barrier on the reaction coordinate. This conclusion is in agreement with the proposal made above that the atom abstraction reactions of $(CH_3)_2S^+-CH_2^•$ occur by a simple radical abstraction mechanism: atom abstraction by neutral alkyl radicals is often associated with significant energy barriers.[22c]

Heat of formation of $(CH_3)_3S^+$ and $(CH_3)_2S^+-CH_2^•$. *Ab initio* molecular orbital calculations were carried out in order to obtain an estimate for the relative stability and the hydrogen atom affinity of $(CH_3)_2S^+-CH_2^•$. Geometry optimization at the UHF/6-31G* level of theory revealed two nearly equally stable structures with C_1 and C_s geometries (Figure 2, a and b, respectively). The absolute energies calculated at the UMP2/6-31G*//UHF/6-31G* + ZPVE level of theory are −515.861 53 hartrees for the C_s geometry (Figure 2b) and −515.862 38 hartrees for the C_1 geometry (when ΔZPVE is taken into account, the latter ion is more stable by 2 kJ mol^{-1}; Figure 2a). The latter value was used to calculate the enthalpy change for an isodesmic reaction involving hydrogen atom abstraction by the more stable conformer of $(CH_3)_2S^+-CH_2^•$ from CH_4 (−40.289 44 hartrees) to yield $(CH_3)_3S^+$ (−516.512 55 hartrees) and $CH_3^•$ (−39.640 79 hartrees). The C−H bond in $(CH_3)_3S^+$ was found to be 4 kJ mol^{-1} stronger than the C−H bond in methane. Combined with the known bond enthalpy of methane

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[25] Sack, T. M.; Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 6795.

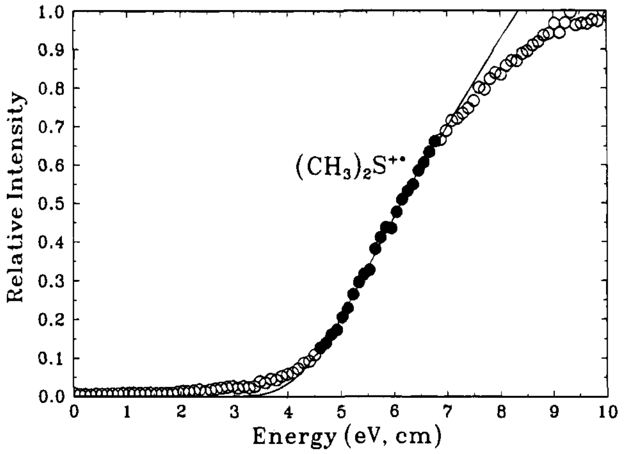

Figure 3. Collision-activated dissociation threshold energy curve for dissociation of $(CH_3)_3S^+$ to $(CH_3)_2S^{\bullet+}$ and $CH_3^\bullet$. The filled circles repesent the range of data that were used to estimate the appearance energy. The convoluted fit is shown by the solid line.

(439 kJ mol^{-1}),[26] this value yields a hydrogen atom affinity of 443 kJ mol^{-1} for the lowest-energy conformer of $(CH_3)_2S^+{-}CH_2^\bullet$. This hydrogen atom affinity is high for an alkyl radical but not for one with a strongly electron-withdrawing substituent. For example, the C−H bond enthalpy in CF_3CH_3 is 446 kJ mol^{-1}.[21] Protonation of methanol increases the C−H bond enthalpy by about 70 kJ mol^{-1}.[21,24]

The heat of formation of $(CH_3)_2S^+{-}CH_2^\bullet$ can be estimated from the calculated C−H bond enthalpy if the heat of formation of $(CH_3)_3S^+$ is known. The differences in the heats of formation of the homologous ions H_3S^+, CH_3SH^+, and $(CH_3)_2SH^+$ can be used to predict a heat of formation of 582 kJ mol^{-1} for $(CH_3)_3S^+$. Semiempirical calculations using the AM1 Hamiltonian place the heat of formation at 607 kJ mol^{-1}. Obviously, an experimental determination is preferable over the above estimates. Hence, the enthalpy change for the dissociation of $(CH_3)_3S^+$ to $(CH_3)_2S^{\bullet+}$ and $CH_3^\bullet$ was determined in a flowing afterglow−triple quadrupole apparatus.[11] This experiment involved methylating dimethyl sulfide in the flow tube of the instrument with $(CH_3)_2F^+$ (generated by self-chemical ionization of fluoromethane). The $(CH_3)_3S^+$ ions were extracted into the triple quadrupole mass analyzer, mass selected with the first quadrupole, and subjected to energy-resolved collision-activated dissocation with argon in the second quadrupole. The reactant and product ions were analyzed with the third quadrupole. A representative plot of the relative abundance of $(CH_3)_2S^{\bullet+}$ versus the center-of-mass collision energy is shown in Figure 3. A threshold energy of 3.4 ± 0.1 eV was obtained from the curves by using an analytical procedure that has been detailed elsewhere.[15] The measured enthalpy change of 331 ± 13 kJ mol^{-1} (at 298 K), together with the known heats of formation of the products,[24] yields a heat of formation of 615 ± 15 kJ mol^{-1} for $(CH_3)_3S^+$.

The measured heat of formation of 615 kJ mol^{-1} for $(CH_3)_3S^+$, together with the calculated hydrogen atom affinity of 443 kJ mol^{-1} for the lowest-energy conformer of $(CH_3)_2S^+{-}CH_2^\bullet$, yields a heat of formation of 840 kJ mol^{-1} for the lowest-energy geometry of the distonic ion $(CH_3)_2S^+{-}CH_2^\bullet$ (Figure 2a). This value places the distonic ion about 74 kJ mol^{-1} higher in energy than the conventional isomer, ionized ethyl methyl sulfide.

Conclusions

The charged radical $(CH_3)_2S^+{-}CH_2^\bullet$ reacts with cyclic alkenes in a manner analogous to that observed for many neutral free radicals: by hydrogen atom abstraction and radical addition. The radical addition reactions observed for $(CH_3)_2S^+{-}CH_2^\bullet$ are rare examples[7] of this type of reactivity for distonic ions. Addition reactions were not observed for the isomeric conventional radical cation, ionized ethyl methyl sulfide.

Molecular orbital calculations predict that hydrogen atom abstraction by $(CH_3)_2S^+{-}CH_2^\bullet$ from the alkenes studied is highly exothermic. However, hydrogen atom abstraction occurs at a low efficiency, suggesting the presence of a significant barrier along the reaction coordinate. The reaction cannot be facilitated by covalent bonding of the neutral reagent at the charge site as is the case for reactions of certain acylium distonic ions, such as $^\bullet CH_2CH_2CH_2C{=}O^+$.[27] Indeed, the reactions of the acylium ions have an order of magnitude greater efficiency. These findings are in agreement with a simple radical abstraction mechanism for hydrogen abstraction by the charged radical.

The odd-spin site of $(CH_3)_2S^+{-}CH_2^\bullet$ dictates its reactivity toward alkenes. This finding parallels those made earlier for the reactions of this charged radical with other types of compounds and provides further support for the description of this species as an electrophilic radical with an inert charge site.

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