The Dimethylene Ketene Radical Cation

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Molecular orbital calculations (at the Becke3LYP/6-31G(d) level of theory) indicate that the distonic ion $^{\bullet}CH_2C(CH_2)CO^+$ is planar and has C_{2v} symmetry. Most of the positive charge resides at the carbonyl carbon while the odd spin is delocalized over the allyl group. A similar spin distribution was calculated for the allyl radical. Hence, the reactivity of $^{\bullet}CH_2C(CH_2)CO^+$ toward spin traps may be expected to resemble that of the neutral allyl radical. This issue was examined experimentally by using Fourier transform ion cyclotron resonance mass spectrometry. Similar to other carbon-centered free radicals, the gaseous $^{\bullet}CH_2C(CH_2)CO^+$ abstracts $H^{\bullet}$ from benzeneselenol, $CH_3Se^{\bullet}$ from dimethyl diselenide, and $I^{\bullet}$ from allyl iodide. However, some of these reactions occur at efficiencies that suggest catalysis by the charged group. Further, the reaction of $^{\bullet}CH_2C(CH_2)CO^+$ with dimethyl disulfide was found to proceed in an unprecedented manner. In addition to the expected formation of $CH_3SCH_2C(CH_2)CO^+$ and $CH_3S^{\bullet}$ (via $CH_3S^{\bullet}$ abstraction), a new distonic ion, $CH_3SCH^{\bullet}C(CH_2)CO^+$, is generated. This ion is likely produced upon $H^{\bullet}$ abstraction by $CH_3S^{\bullet}$ from $CH_3SCH_2C(CH_2)CO^+$ within the collision complex (net CH_2S abstraction). The latter reaction has not been reported for distonic radical cations with localized radical sites. Hence, the reaction must be driven by the regeneration of the delocalized allylic radical. This proposal is supported by the observation of CH_2S abstraction for the product ion $CH_3SCH^{\bullet}C(CH_2)CO^+$ that also contains a delocalized radical site.

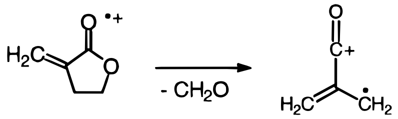
Introduction

A large number of structural variations exist for distonic radical cations (ionized zwitterions, biradicals, and ylides).[1−3] However, current knowledge concerning the *reactivity* of these radical cations is largely based on the examination of species where both the charge and unpaired spin are localized on specific atoms in the ion.[3]

The dimethylene ketene radical cation ($^{\bullet}CH_2C(CH_2)CO^+$) is a distonic ion with a potential for delocalization of both charge and spin. This species was first reported in 1982 by Burgers et al. to be formed upon fragmentation of ionized α-methylene-γ-butyrolactone (Scheme 1).[4] Collision-activated dissociation of $^{\bullet}CH_2C(CH_2)CO^+$ yields fragments, most notably the allene radical cation, that are consistent with the proposed structure and that distinguish the ion from 14 other $C_4H_4O^{\bullet+}$ isomers.[4,5] The heat of formation of $^{\bullet}CH_2C(CH_2)CO^+$ has been determined by appearance energy measurements to be 198 ± 2 kcal mol^{-1}.[4] However, the reactivity of this ion has not been systematically examined.

Since the dimethylene ketene radical cation contains a relatively unreactive acylium charge site,[6] this species provides an excellent tool for probing the effects of spin delocalization on radical-type reactions of distonic ions. We report herein the reactivity of this ion toward various reagents. In conjunction with experimental work, molecular orbital calculations were conducted to gain further insight into the structure and properties of $^{\bullet}CH_2C(CH_2)CO^+$.

Scheme 1



Experimental Section

All the experiments were carried out in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR) described previously.[7] This instrument consists of a differentially pumped dual cell which is placed within the magnetic field produced by a 3.0 T superconducting magnet operated at 2.2−2.7 T. The nominal base pressure is less than 10^{-9} Torr, as maintained by two Balzer turbomolecular pumps (330 L s^{-1}), each backed with an Alcatel mechanical pump. The reagents were introduced into the instrument by using a Varian leak valve or two Extrel-manufactured heated batch inlet systems equipped with variable leak valves. The typical nominal operating pressure in each cell was about 1×10^{-7} Torr, as measured by an ionization gauge located on each side

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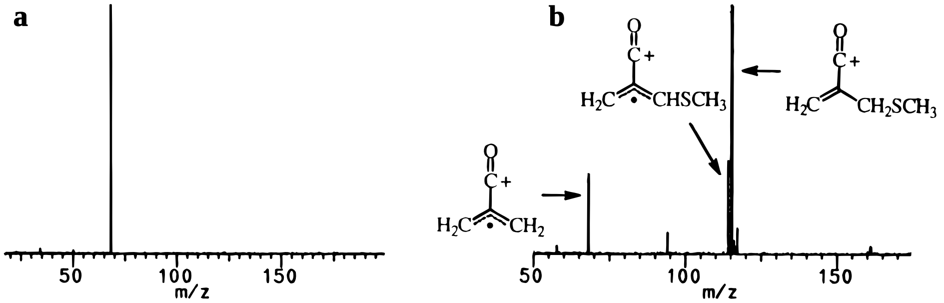


Figure 1. (a) Isolation of the dimethylene ketene radical cation and (b) its reaction with dimethyl disulfide.

of the dual cell. All reagents were obtained commercially and checked for purity by gas chromatography and by mass spectrometry.

The ions were generated by electron ionization in one side of the dual cell. The ion signal was optimized for each experiment by varying the electron current (4−8 μA), electron energy (40−70 eV), and duration of the electron beam (25−70 ms). After generation, the ions were transferred into the other side of the dual cell through a 2 mm hole in the plate common to the cells (the conductance limit plate) by grounding this plate for 70−100 μs. *Prior to* the transfer event, ions in the receiving cell were removed by applying a negative potential to the remote trapping plate of this cell for 10−15 ms. At all other times, the three trapping plates were kept at +2 V. The transferred ions were internally and translationally cooled by collisions with argon pulsed into the cell at a maximum nominal pressure of approximately 1×10^{-5} Torr.

After cooling the ions, stored-waveform inverse Fourier transform excitation pulses[8] were applied to the excitation plates of the cell to eject unwanted ions (Extrel FTMS SWIFT module). The isolated ion was allowed to react with the desired neutral reagent (the only neutral reagent present in this cell) for a variable period of time. Primary product ions were identified based on their fixed branching ratios at short reaction times. In some instances, secondary product ions were identified by isolating the primary product ions and examining their reactions with the neutral reagent. All the spectra discussed are an average of at least 50 acquisitions obtained using “chirp” or SWIFT excitation (0.5 cm final radius for all ions). The spectra were recorded as 32 k or 64 k data points and subjected to one zero fill *prior to* Fourier transformation.

Since the reactions studied under the conditions described above follow pseudo-first-order kinetics, the second-order rate constant (k_{exp}) of each reaction was obtained from a semilogarithmic plot of the relative abundance of the reactant ion versus time. The ion gauges were calibrated for each neutral reagent by using a literature procedure.[9,10] A correction factor for the pressure gradient between the cell and the ion gauge was obtained by examination of well-characterized reactions with known rate constants involving each neutral reagent. The collision rate constants ($k_{\mathrm{collision}}$) were calculated using the parameterized trajectory theory.[11] Total reaction efficiencies are given as $k_{\mathrm{exp}}/k_{\mathrm{collision}}$. The detection limit for observing a reaction is estimated to correspond to an efficiency of 0.001 in these experiments. The precision of the rate constant measurements was better than +10%. A conservative estimate for the accuracy of these values is ±50% (the largest source of error in these experiments arises from the estimated pressure of the neutral reagent).

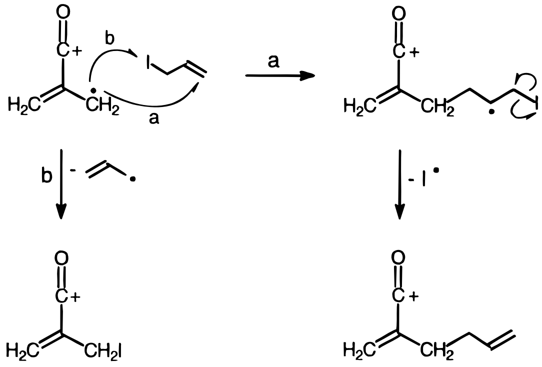
Molecular orbital calculations using density functional theory (DFT) were performed on an IBM RISC 6000 550L workstation by using the Gaussian 92 Revision F suite of programs.[12a] The geometries were fully optimized at the Becke3LYP/6-31G(d) level of theory. Zero-point vibrational energies (ZPVE) were calculated from the harmonic frequencies and scaled by a factor of 0.9804 to account for the systematic overestimation of the vibrational frequencies by the density functional method.[12b] The force constant matrixes obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures).

Table 1. Reaction Products, Their Branching Ratios, and the Reaction Efficiencies (% collisions leading to reaction) for the Reactions of the Dimethylene Ketene Radical Cation with Selected Neutral Reagents

neutral reagent	efficiency[a]	products
CH_3SSCH_3	0.66	$CH_3SCH_2C(CH_2)CO^+$ (86%) $CH_3SCH^{\bullet}C(CH_2)CO^+$ (14%)
$CH_3SeSeCH_3$	0.61	$CH_3SeCH_2C(CH_2)CO^+$ (100%)
$CH_2{=}CHCH_2I$	$<<0.1$	$CH_2{=}CHCH_2CH_2C(CH_2)CO^+$ (33%) $ICH_2C(CH_2)CO^+$ (67%)
C_6H_5SeH	0.34	$C_6H_5CH_2C(CH_2)CO^+$ (20%) $CH_3C(CH_2)CO^+$ (80%)

[a] Efficiency = $k_{\mathrm{exp}}/k_{\mathrm{coll}}$

Scheme 2



Results and Discussion

Computational Results. Molecular orbital calculations based on density functional theory were performed on $^{\bullet}CH_2C(CH_2)CO^+$ in order to gain insight into the extent of charge and/or spin delocalization in this ion. At the Becke3LYP/6-31G(d) level of theory, $^{\bullet}CH_2C(CH_2)CO^+$ was found to be planar with C_{2v} symmetry. The natural charge[12] at the acylium carbon in $^{\bullet}CH_2C(CH_2)CO^+$ (+0.94)

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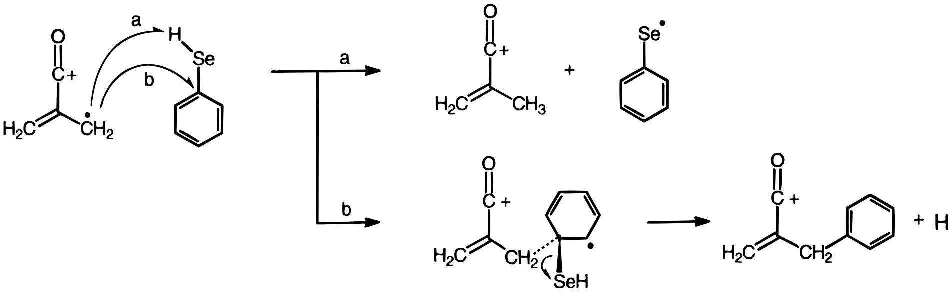
Scheme 3



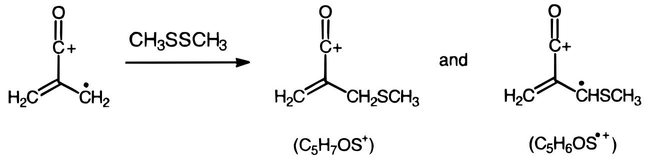
was calculated to be the same as that at the acylium carbon in $CH_3C(CH_2)CO^+$ (+0.92) and $^{\bullet}CH_2CH_2CH_2CO^+$ (+0.94). The positive charge calculated for the methylene groups in $^{\bullet}CH_2C(CH_2)CO^+$ (+0.32) is less than that of the methylene group in $CH_3C(CH_2)CO^+$ (+0.40) and the allyl cation (+0.53), but greater than the charge at the terminal methylene group in $^{\bullet}CH_2CH_2CH_2CO^+$ (+0.16) and in the allyl radical (+0.04). The spin density at each methylene carbon in $^{\bullet}CH_2C(CH_2)CO^+$ (0.64e) is roughly equivalent to that calculated for the allyl radical (0.72e at each terminal carbon), but substantially less than the spin density at the formal radical site in $^{\bullet}CH_2CH_2CH_2CO^+$ (0.95e). Hence, $^{\bullet}CH_2C(CH_2)CO^+$ can be viewed as a delocalized, electron deficient allyl radical. The cyclopropyl ketene radical cation $(CH_2)_2C{=}C{=}O^{+\bullet}$, a ring-closed isomer of $^{\bullet}CH_2C(CH_2)CO^+$, was calculated to lie 14 kcal/mol higher in energy (at Becke3LYP/6-31G(d) + ZPVE).

Reactions of $^{\bullet}CH_2C(CH_2)CO^+$. The acylium charge site in gas-phase ions has been found to be relatively unreactive.[3b−d,6] Hence, the reactions of $^{\bullet}CH_2C(CH_2)CO^+$ can be expected to predominantly involve the radical site. This prediction was probed by exploring the gas-phase reactivity of $^{\bullet}CH_2C(CH_2)CO^+$ toward allyl iodide, benzeneselenol, dimethyl disulfide (Figure 1), and dimethyl diselenide.

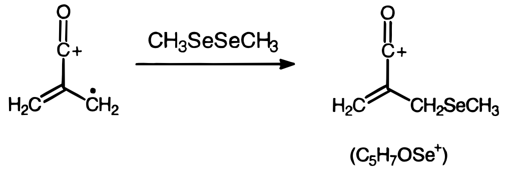
The reaction of $^{\bullet}CH_2C(CH_2)CO^+$ with allyl iodide occurs by predominant iodine atom abstraction (67% of the product distribution). This reaction is commonly observed for neutral carbon-centered free radicals.[13] In addition to iodine atom abstraction, a slower allyl radical abstraction also takes place (33%; Table 1; this reaction likely occurs via an addition−elimination mechanism; Scheme 2). Similar product distributions have been reported for gaseous distonic ions with localized radical sites. For example, $^{\bullet}CH_2CH_2CH_2CO^+$ reacts with allyl iodide via iodine (86%) and allyl abstraction (14%).[14] However, the reaction of this ion occurs at a significantly greater efficiency (the efficiency is 0.45 for $^{\bullet}CH_2CH_2CH_2CO^+$ and ≪0.1 for $^{\bullet}CH_2C(CH_2)CO^+$), which may partially be explained by the localized radical site of this species.

The ion $^{\bullet}CH_2C(CH_2)CO^+$ reacts with benzeneselenol, a very efficient hydrogen atom donor, by the expected facile hydrogen atom abstraction (80%) (Scheme 3; Table 1). Slow phenyl abstraction was also observed (20%; a possible mechanism is shown in Scheme 3). This reaction has not been reported before.[3c,15,16]

Scheme 4



Scheme 5



Dimethyl disulfide readily transfers $CH_3S^{\bullet}$ to various neutral and ionic radicals but abstracts an electron from most conventional radical cations if the reaction is exothermic.[3c−d,6] CH_3S-transfer takes place for $^{\bullet}CH_2C(CH_2)CO^+$ (86%; Figure 1b).[17] In addition, a minor channel corresponding to CH_2S transfer was observed (14%; Scheme 4; Table 1; Figure 1b). In contrast, dimethyl diselenide reacts with $^{\bullet}CH_2C(CH_2)CO^+$ by the expected, exclusive $CH_3Se^{\bullet}$ transfer (Scheme 5; Table 1).

To confirm that the observed reactivity is due to reactions at the radical site of $^{\bullet}CH_2C(CH_2)CO^+$, control experiments were conducted wherein the even-electron analogues $CH_3C(CH_2)CO^+$ and c-$C_3H_5CO^+$ (generated from the corresponding acyl chlorides) were allowed to react with the spin traps discussed above. Both of these ions are unreactive toward every reagent studied. Hence, the reactions observed for $^{\bullet}CH_2C(CH_2)CO^+$ occur via bond formation at the radical site rather than the charge site.

Mechanisms of the Radical Reactions of $^{\bullet}CH_2C(CH_2)CO^+$. Simple gas-phase radical abstraction reactions are generally much slower (efficiencies < 0.1) than ionic reactions.[3d,18] This is demonstrated, for example, by the low rates of iodine abstraction from allyl iodide by $^{\bullet}CH_2C(CH_2)CO^+$ (efficiency ≪ 0.1; Table 1) and of $CH_3S^{\bullet}$ abstraction from dimethyl disulfide by the coordinatively saturated distonic ion $^{\bullet}CH_2S^+(CH_3)_2$ (efficiency

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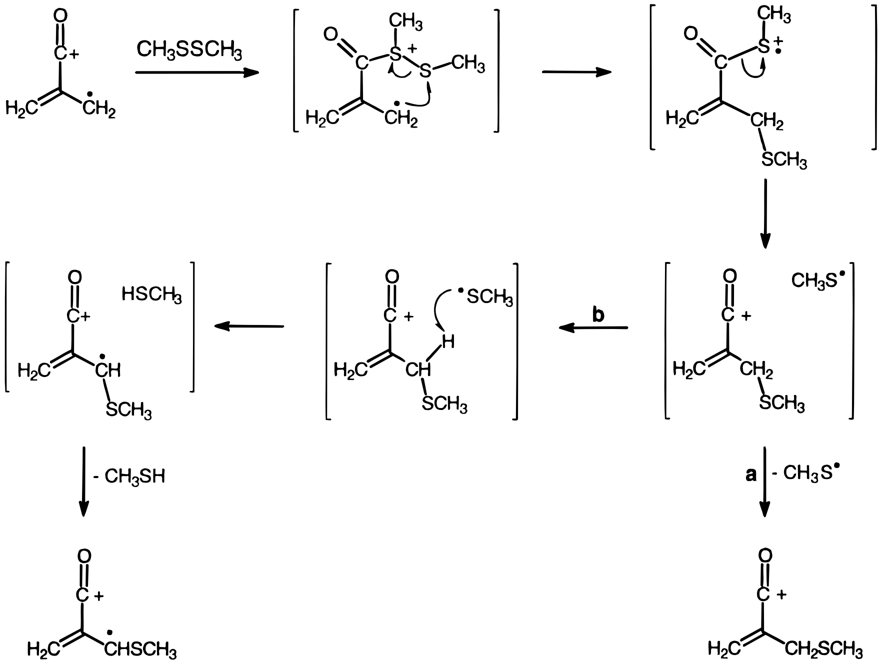
Scheme 6



0.05).[19] In sharp contrast, the reaction of ${}^\bullet CH_2C(CH_2)CO^+$ with dimethyl disulfide occurs nearly at collision rate (eff = 0.66; Table 1). Hence, this reaction probably involves active participation of the charge site (*charge catalysis mechanism*).[3b−d,6,14]

A nucleophilic reagent, such as dimethyl disulfide, can form a relatively strong bond to the acylium carbon of ${}^\bullet CH_2C(CH_2)CO^+$, which lowers the energy of the collision complex. This bond formation likely positions dimethyl disulfide in a favorable orientation for intramolecular $CH_3S^\bullet$ transfer to the radical-bearing carbon (Scheme 6), thus facilitating the reaction. A similar situation probably applies for $CH_3Se^\bullet$ abstraction from dimethyl diselenide and hydrogen atom abstraction from benzeneselenol since these processes also occur at very high efficiencies (the efficiencies are 0.61 and 0.34, respectively; Table 1). In contrast, bond formation between the acylium charge site and either the allyl moiety or the iodine atom of allyl iodide does not result in significant acceleration of the reaction with allyl iodide. Hence, these bonding interactions either do not form a long-lived molecule or position the neutral reagent unfavorably for a subsequent iodine atom transfer to the radical site.

Generation of Novel Distonic Ions upon Reaction of ${}^\bullet CH_2C(CH_2)CO^+$ with Dimethyl Disulfide. A minor but remarkable exit channel (14%) for the collision complex of ${}^\bullet CH_2C(CH_2)CO^+$ with dimethyl disulfide corresponds to formal CH_2S abstraction by the ion (Scheme 6, path b; Table 1). This reaction likely occurs via $H^\bullet$ abstraction by the major neutral reaction product, $CH_3S^\bullet$, from the allylic position of the ionic product $CH_3SCH_2C(CH_2)CO^+$ before dissociation of the ion−molecule complex. Hence, the reaction *regenerates a delocalized allylic radical* ($C_5H_6OS^{\bullet +}$; Scheme 6, path b). The reaction is likely to be exothermic (the homolytic S−H bond dissociation energy[19a] in CH_3S-H, 87.4 kcal/mol, exceeds the homolytic C−H bond dissociation energy[19b] of the allylic position of, for example, 1-butene, 82.5 kcal/mol, and hence most likely also that in $CH_3SCH_2C(CH_2)CO^+$). However, this is not the case for $H^\bullet$ abstraction from a saturated carbon (e.g., the homolytic C−H dissociation bond energy[19b] at the methyl carbon in *n*-propane is 98.2 kcal/mol, i.e., significantly greater than the S−H bond dissociation energy[19] in CH_3S-H). Delocalization of the radical site provides an important driving force for this reaction. Hence, it is not surprising that CH_2S abstraction has not been observed for distonic ions with localized radical sites. Finally, the complete absence of CH_2Se abstraction for dimethyl diselenide is likely explained by the weakness of selenium−hydrogen bonds,[16,19a] which makes $H^\bullet$ abstraction by $CH_3Se^\bullet$ less exothermic than by $CH_3S^\bullet$.

The structure of the product ion formed upon CH_2S abstraction ($C_5H_6OS^{\bullet +}$) was examined by isolating the ion and allowing it to react with dimethyl disulfide. The ion displays behavior similar to that of ${}^\bullet CH_2C(CH_2)CO^+$, i.e., the reaction occurs by predominant $CH_3S^\bullet$ abstraction (to yield $C_6H_9OS_2{}^+$) accompanied by a slow CH_2S abstraction (to yield $C_6H_8OS_2{}^{\bullet +}$; Scheme 7; Table 2). The observation of $CH_3S^\bullet$ abstraction demonstrates that the reactant ion is a distonic ion, and hence provides strong support for the proposed structure $CH_3SCH^\bullet C(CH_2)CO^+$.

Two isomeric structures are possible for the two product ions obtained upon reaction of dimethyl disulfide with the CH_2S abstraction product of ${}^\bullet CH_2C(CH_2)CO^+$. The ions with the structures shown in Scheme 7 are likely to be the kinetically favored products because they result from $CH_3S^\bullet/CH_2S$ transfer to the less hindered terminal carbon. Examination of the reaction of the isolated CH_2S abstraction product ($C_6H_8OS_2{}^{\bullet +}$; likely to have the structure $CH_3SCH^\bullet C(CHSCH_3)CO^+$) with dimethyl disulfide confirms that the reactant is a distonic ion, as the reaction occurs by exclusive $CH_3S^\bullet$ abstraction (to yield $C_7H_{11}OS_3{}^+$; Scheme 8; Table 2). However, the reaction occurs at a much lower efficiency than that of

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Scheme 7

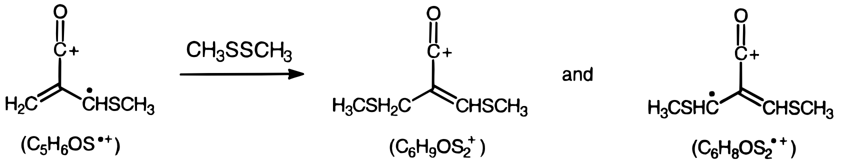


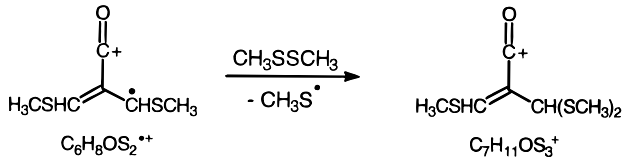
Table 2. Reaction Products, Their Branching Ratios, and the Reaction Efficiencies (% collisions leading to reaction) for the Reactions of the Product Ions $C_5H_6OS^{\bullet+}$ and $C_6H_8OS_2^{\bullet+}$ with Dimethyl Disulfide

ion	neutral reagent	efficiency[a]	products
$C_5H_6OS^{\bullet+}$	CH_3SSCH_3	0.11	$C_6H_9OS_2^+$ (41%) $C_6H_8OS_2^{\bullet+}$ (59%)
$C_6H_8OS_2^{\bullet+}$	CH_3SSCH_3	0.017	$C_7H_{11}OS_3^+$ (100%)

[a] Efficiency = $k_{\mathrm{exp}}/k_{\mathrm{coll}}$.

$^{\bullet}CH_2C(CH_2)CO^+$ and $CH_3SCH^{\bullet}C(CH_2)CO^+$ (the efficiencies for the reaction of $C_4H_4O^{\bullet+}$, $C_5H_6OS^{\bullet+}$, and $C_6H_8OS_2^{\bullet+}$ with dimethyl disulfide are 0.66, 0.11, and 0.017, respectively). This gradual decrease in reactivity upon addition of one and two thiomethyl groups likely arises from enhanced stabilization of the radical site by the thiomethyl groups and possibly also from increased steric hindrance. Steric hindrance probably also explains the absence of CH_2S abstraction for the largest ion.

Scheme 8



Conclusions

Computational and experimental examination of the properties of the gaseous dimethylene ketene radical cation, $^{\bullet}CH_2C(CH_2)CO^+$, supports its description as a delocalized, electron deficient allyl radical. This species is calculated to carry most of the positive charge at the carbonyl carbon, while the spin distribution is nearly identical to that of the neutral allyl radical. As expected, $^{\bullet}CH_2C(CH_2)CO^+$ reacts via typical radical pathways although covalent bonding at the charge site apparently facilitates some of these reactions. The ion reacts with dimethyl disulfide to yield new thiomethyl-containing distonic ions. These reactions are driven by regeneration of the delocalized allyl radical, and hence are not observed for distonic ions with localized radical sites.

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