

The Acyclic Distonic Isomer of Ionized Cyclopentanone: •CH₂CH₂CH₂CH₂CO⁺

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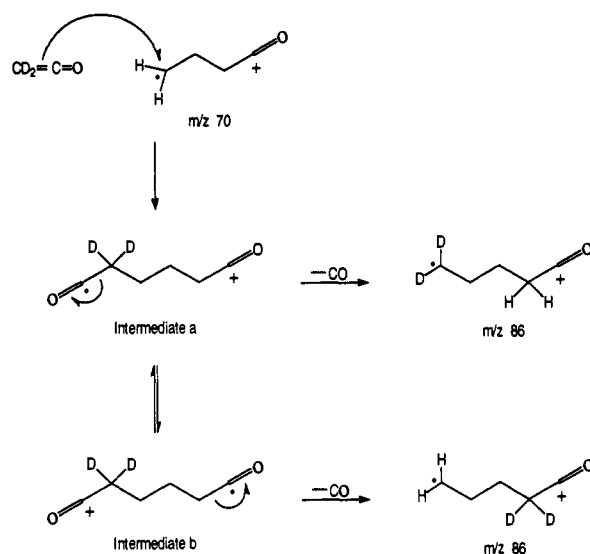
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Distonic radical cations,¹ ions with spatially separated charge and radical sites, have been of wide interest since it was realized that these ions are generated by rearrangement of low-energy, long-lived radical cations in the condensed phase as well as in the gas phase.²⁻⁴ A thoroughly studied^{5,6} example is the radical cation of cyclobutanone, which was recently demonstrated^{5c} to have the acyclic γ -distonic structure •CH₂CH₂CH₂CO⁺. This ion is the longest-chain stable distonic ion reported to date.^{2,4} We discuss here our initial results on the gas-phase reaction of •CH₂CH₂CH₂CO⁺ with ketene which yields the acyclic isomer of ionized cyclopentanone, •CH₂CH₂CH₂CH₂CO⁺. This ion is the first known stable δ -distonic ion.

All experiments were carried out in a dual-cell Fourier-transform ion cyclotron resonance mass spectrometer (Extrel Model 2001 FT/MS) described^{6,7} in detail elsewhere. The ion •CH₂CH₂CH₂CO⁺ was generated by electron ionization of cyclobutanone in one side of the dual-cell reaction chamber. The ions formed upon ionization were transferred into the other side of the dual cell, and •CH₂CH₂CH₂CO⁺ was isolated by ejecting all other ions from the cell. Upon reaction with ketene, •CH₂CH₂CH₂CO⁺ yields a radical cation of m/z 84 (an even-electron ion of m/z 83 is also formed; the total reaction efficiency, or $k_{\text{observed}}/k_{\text{collision}}$, is 0.2).⁸ Exact mass measurement verified the elemental composition of the new radical cation to be C₅H₈O. Thus, this ion is generated by elimination of CO from the collision complex.

Transfer of CH₂ from ketene to distonic ions is thought to involve radical addition to the terminal carbon of ketene followed by loss of CO.⁹ For the reaction of •CH₂CH₂CH₂CO⁺ with ketene, this mechanism would lead to •CH₂CH₂CH₂CH₂CO⁺ as the initial product (Scheme 1). If •CH₂CH₂CH₂CH₂CO⁺ was indeed generated, it was expected to cyclize and yield ionized cyclopentanone as the final product. In order to determine whether the new C₅H₈O⁺ ion is ionized cyclopentanone, its reactions were examined in the FT-ICR. For these studies, the C₅H₈O⁺ ion was generated in one side of the dual-cell by reaction of ionized cyclobutanone with ketene and transferred into the other cell for reactions with neutral reagents. In order to avoid interference from an isomeric ion with an unknown structure generated upon reaction of •CH₂CH₂CH₂CO⁺ with neutral cyclobutanone, deuterated ketene was used instead of ketene. Deuterated ketene yields an ion C₅H₆D₂O⁺ (m/z 86) with a different mass value than the ion (m/z 84) formed in the

Scheme 1



interfering •CH₂CH₂CH₂CO⁺/cyclobutanone reaction. The latter ion, together with all other undesired ions, was ejected from the reaction chamber prior to reaction studies.

Collision-activated dissociation of the new C₅H₈O⁺ ion did not produce structurally informative data. Therefore, ion-molecule reactions were examined. Earlier work¹⁰ shows that abstraction of CH₃S• from dimethyl disulfide is indicative of a distonic structure for the reactant ion. For example, the well-characterized^{2,4-6,11} ions •CH₂CH₂CO⁺ and •CH₂CH₂CH₂CO⁺ undergo this reaction (efficiency 0.06 and 0.3, respectively). In contrast, conventional radical cations either are unreactive or react with dimethyl disulfide by exclusive electron transfer.^{4,6,10} Most importantly, all the C₅H₈O⁺ ions studied to date¹⁰ undergo charge exchange with dimethyl disulfide, including ionized cyclopentanone (Figure 1) and the ion generated upon reaction of •CH₂CH₂CH₂CO⁺ with neutral cyclobutanone. However, the new radical cation formed in the ketene reaction does not undergo electron transfer with dimethyl disulfide: abstraction of CH₃S• is the only reaction observed (efficiency 0.02; Figure 1). This finding conclusively demonstrates that the new ion has a distonic structure.

In order to learn more about the properties of the new distonic ion, its recombination energy was probed using reagents with low ionization energies, such as trimethylamine (IE = 7.8 eV) and *N,N*-dimethylaniline (IE = 7.12 eV).¹² Exothermic electron transfer within a long-lived ion-molecule collision complex is known to proceed rapidly in the gas phase.¹³ However, the new distonic ion does not react by electron transfer with neutral molecules. This is true even for *N,N*-dimethylaniline (slow deprotonation is the only reaction observed), which suggests that the recombination energy of the ion is less than 7.12 eV. This value is unusually low for an organic radical cation.^{12,14,15} However, acylium ions have low recombination energies: that of CH₃CO⁺ is only 7.0 eV.¹⁴ Hence, a recombination energy of less

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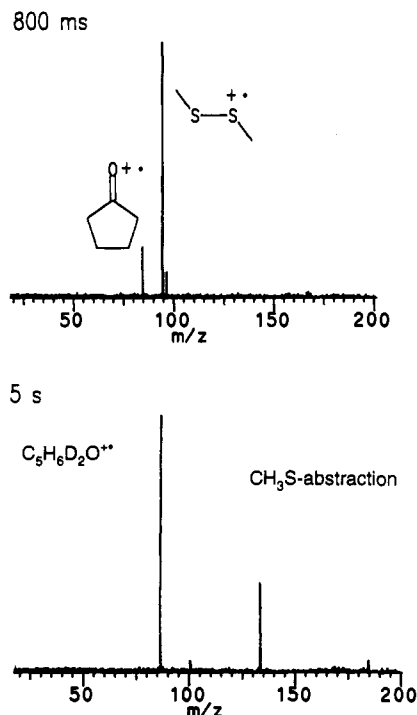


Figure 1. Reaction of neutral dimethyl disulfide (nominal pressure 1.2×10^{-7} Torr) with (top) ionized cyclopentanone and (bottom) the new radical cation generated upon reaction of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ with ketene.

than 7.12 eV is in excellent agreement with the acylium distonic structure $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ for the ion of interest. The assigned structure is also consistent with the acidity of the ion. The acidity was bracketed^{12,16} between 200.6 and 201.4 kcal/mol by allowing the ion to react with reference bases.¹⁷ This value is comparable to the acidity of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ (201–202 kcal/mol).¹⁸

The complete lack of electron-transfer reactions for the ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ demonstrates that this ion does not exist

(15) $\Delta H_f(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}=\text{O}^{\cdot+}) \approx 163$ kcal/mol; IE ≈ 8.65 eV as estimated using the following values (ref 12b): $\text{CH}_3\text{CH}=\text{C}=\text{O}$, IE = 8.95 eV; $\text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{O}$, IE = 8.80 eV.

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(17) Proton transfer occurs to cyclohexanone (PA = 201.4 kcal/mol) but not to molecules with lower proton affinities than 200.6 kcal/mol (e.g., dimethyl sulfide).

(18) Acidity estimated on the basis the following proton affinities: 198 kcal/mol (ref 12b), 199.4 kcal/mol (ref 12b), and ≤ 201.4 kcal/mol (proton transfer occurs to cyclohexanone) for CH_3CO^+ , $\text{CH}_3\text{CH}_2\text{CO}^+$, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$, respectively.

in equilibrium with any conventional $\text{C}_5\text{H}_8\text{O}^{\cdot+}$ ion. Hence, the ion is stable toward cyclization to form ionized cyclopentanone, as well as toward hydrogen atom shifts which would yield $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}=\text{O}^{\cdot+}$.¹⁵ Examination of $\text{CH}_3\text{CH}^{\cdot}\text{CH}_2\text{CH}_2\text{CO}^+$ rules out the occurrence of 1,2-hydrogen shifts in $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ as the former ion shows charge exchange with dimethyl disulfide (accompanied by CH_3S abstraction; similar reactivity has been observed^{5c} also for another γ -distonic ion: $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$).

Finally, the mechanism for the formation of the ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ was probed by using ^{18}O -labeled cyclobutanone and CD_2CO . Radical addition of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ to the terminal carbon of ketene would yield a symmetrical intermediate. The use of either $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^{18}\text{O}^+$ or CD_2CO should then produce two unsymmetrical intermediates¹⁹ (a and b; Scheme 1) and result in two different product ions. The reaction of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^{18}\text{O}^+$ with CH_2CO indeed yields an equal amount of each of two product ions, $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^{16}\text{O}^+$ (m/z 84) and $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^{18}\text{O}^+$ (m/z 86). This finding verifies the involvement of a symmetrical intermediate with an equal probability of losing either C^{16}O or C^{18}O , and it therefore provides strong support for the proposed mechanism. Further support is obtained from the reaction of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ with CD_2CO , which should generate two isomeric product ions of m/z 86, one with hydrogen and one with deuterium atoms at the most acidic site (α to the carbonyl carbon, Scheme 1). Both of these product ions are formed, as demonstrated by transfer of H^+ together with D^+ from the ions to basic molecules.

In conclusion, the radical cation $\text{C}_5\text{H}_8\text{O}^{\cdot+}$ generated upon reaction of $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ with neutral ketene is a ring-opened isomer of ionized cyclopentanone: $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$. This distonic ion, with three heavy atoms separating the charge and the odd spin sites, is the longest-chain long-lived distonic ion known to date. The ion $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}^+$ is stable toward cyclization²⁰ as well as isomerization by hydrogen shifts.

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