Scheme I, hydrogen atom abstraction from **1** by the putative iron-oxo species would give radical **2**, which can ring open to radical **3** ($k = 2 \times 10^{11}$ s^{-1} at 30 °C);[13] subsequent hydroxyl transfer from the Fe(IV) species to **3** (oxygen rebound) would give product **4**. This mechanism was further supported by the observed kinetic isotope effect of 7.8 when the monodeuteriomethyl derivative of **1** was used as substrate, and it suggested only a tentative limit of $< 4 \times 10^9$ s^{-1} for the rate constant for the oxygen rebound step.[14] Nevertheless, the simple preparation of **1**, the easy recovery of **1** and its products from the reaction medium, and the apparent regiospecific oxidation of **1** suggest that aryl-containing cyclopropanes will be useful for study of various monooxygenases and their models.[16]

Supplementary Material Available: Physical constants (^{1}H NMR, HRMS) for the epoxides and detailed procedures for the preparation of **1** and **4** (6 pages). Ordering information is given on any current masthead page.

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[13] Newcomb, M.; Manek, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 9662.

[14] A rate constant of 2×10^{10} s^{-1} has been estimated for rebound in P-450 oxidation,[5e,15] but rebound in MTM oxidation appears to be slower.[2f]

[15] Bowry, V. W.; Lusztyck, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1989**, *111*, 1927.

[16] Castellino and Bruice had reported that (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene was oxidized by a P-450 model to the corresponding (*trans*-2,*trans*-3-diphenylcyclopropyl)carbinyl radical to homoallyl radical with the radical rearrangement estimated as $\geq 2 \times 10^{10}$ s^{-1} (Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512).

[17] This research was supported by NSF grants to M.N. (CHE8816365) and C.-H.W. (CHE8996249). We thank Dr. M. B. Manek for assistance with the synthesis of **1**.

Radical Type Reactivity in a γ-Distonic Radical Cation: A Gas-Phase Experimental Study

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In sharp contrast to the extensive work carried out on radical cations that are generated by removal of an electron from a stable, neutral molecule,[1] ions with *spatially separated radical and charge sites* (distonic ions[2]) have only recently become the focus of attention. Interest in these ions was sparked by the discovery[3] that they can be more stable than their conventional isomers. Reactions of various ions with the radical and charge sites formally on adjacent atoms (α-distonic ions) have been investigated in detail.[2] However, it is difficult to distinguish the role of the charge and radical sites in these reactions.[4] The current knowledge on distonic ions with the charge and radical sites separated by at least one heavy atom is almost exclusively limited to unimolecular chemistry of highly excited and short-lived species.[2] The results obtained thus far on bimolecular reactions of low-energy β-distonic ions suggest that they predominantly involve the charge site,[2,4,5] although some recent results[4b] could also be explained in terms of a radical type mechanism. We report here the first study on the bimolecular gas-phase reactions of a stable γ-distonic ion. Conclusive evidence is presented for a radical type reaction occurring remotely from the charge site.

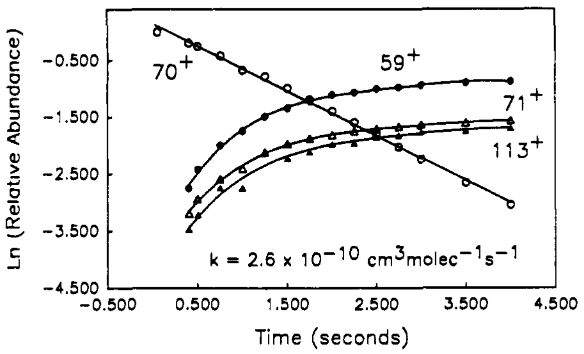
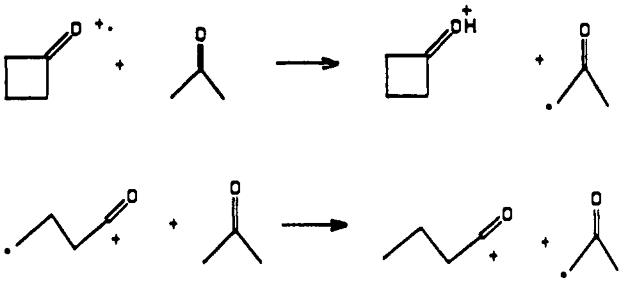


Figure 1. Reaction of ionized cyclobutanone with acetone (9×10^{-8} Torr).

Scheme I



Ionized cyclobutanone was recently suggested[6] to have the γ-distonic, open-chain structure $^{\bullet}CH_2CH_2CH_2C{=}O^+$. We observed that this ion abstracts a hydrogen atom from acetone in a dual-cell Fourier transform ion cyclotron resonance instrument (a prototype Extrel FTMS-2001).[7] The product ion (*m*/*z* 71) corresponds to 30% of the total product ion distribution; other major ionic products include protonated acetone (*m*/*z* 59, 50%) and an ion (*m*/*z* 113, 20%) formed by loss of a methyl radical from the complex of ionized cyclobutanone and acetone (Figure 1). For d_6-acetone, abstraction of a deuterium atom by ionized cyclobutanone to yield a positive ion of *m*/*z* 72 was observed, in addition to protonated d_6-acetone (*m*/*z* 65) and an ion of *m*/*z* 116. Great care was taken to avoid protonation of neutral cyclobutanone since protonated cyclobutanone has the same mass value as the reaction product of interest (*m*/*z* 71). Cyclobutanone was introduced into one of the differentially pumped reaction regions (cell 1) for the ionization event only (pulsed sample introduction[8]). After electron ionization, ionized cyclobutanone was transferred into the other reaction region (cell 2), where it was allowed to react with acetone. No neutral cyclobutanone was in the instrument at this time. A double-resonance experiment that involved ejection of ionized cyclobutanone from the cell confirmed that this ion was the origin of all the product ions mentioned above.

Assuming that ionized cyclobutanone has the proposed[6] acyclic structure (calculated[6b] to be 18 kcal/mol lower in energy than the cyclic structure), the observed hydrogen atom abstraction from acetone represents the first radical type reaction observed for a γ-distonic radical cation in the gas phase. However, no conclusive experimental evidence existed at the time of this work for the proposed acyclic structure.[9] Hydrogen atom abstraction from acetone would be near thermoneutral for the original cyclic structure[10,11] as well as for the acyclic structure.[11,12] Our results

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[1] See, for example: Hammerich, O.; Parker, V. D. *Phys. Org. Chem.* **1984**, *20*, 55.

[2] A review: Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

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

[4] (a) Rusli, R. D.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 535. (b) Wittneben, D.; Grutzmacher, H.-F. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 545. (c) De Koster, C. G.; Van Houte, J. J.; Van Thuijl, J. *Int. J. Mass Spectrom. Ion Processes* **1990**, *98*, 235.

[5] Zeller, L.; Farrell, J.; Vainiotalo, P.; Kenttämaa, H. I., submitted for publication.

[6] (a) Heinrich, N.; Koch, W.; Morrow, J. C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 6332. (b) Dass, C.; Gross, M. L. *Org. Mass Spectrom.* **1990**, *25*, 24.

[7] Farrell, J. T., Jr.; Lin, P.; Kenttämaa, H. I. *Anal. Chim. Acta* **1991**, *246*, 227.

[8] Carlin, T. J.; Freiser, B. F. *Anal. Chem.* **1983**, *55*, 571.

[9] Rearrangement of $^{\bullet}CH_2CH_2CH_2C{=}O^+$ to $CH_3CH_2CH{=}C{=}O^{\bullet+}$ can be ruled out: $H^{\bullet}$ abstraction from acetone and protonation of acetone would be endothermic for this structure (≥ 3 kcal/mol[11,12]) (for $CH_3CH{=}C{=}O^{\bullet+}$, $\Delta H_{rxn} \geq 0$ kcal/mol for both reactions).

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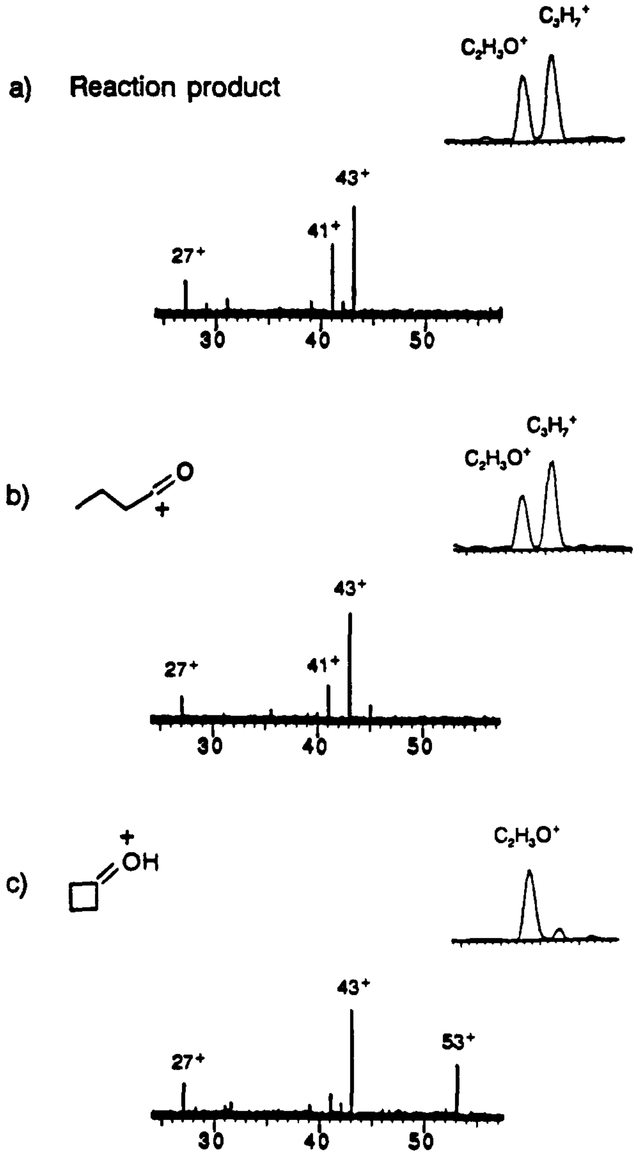

Figure 2. Collision-activated dissociation spectra for (a) ionized cyclobutanone after abstraction of a hydrogen atom from acetone (the reaction product), (b) butanoyl reference ion obtained by loss of a methyl radical from ionized 2-pentanone, and (c) protonated cyclobutanone. The estimated ion kinetic energy is 30–50 eV. Only protonated cyclobutanone loses water to yield a fragment ion of *m/z* 53 upon collisional activation. The insert near each spectrum shows an enlargement of the spectral region at *m/z* 43: the acyclic isomer produces two isobaric ions at this nominal mass value ($C_3H_7^+$ and $C_2H_3O^+$), while the cyclic ion yields predominantly $C_2H_3O^+$.

suggest that only *one* ion structure is involved in the reaction (e.g., linear decay of ionized cyclobutane, Figure 1). If ionized cyclobutanone has an open-chain structure, the barrier for ring opening must be below 17 kcal/mol since the same product distribution is obtained for cyclobutanone ionized by 60-eV electron ionization and by charge exchange with $CS_2^{\bullet+}$ ($\Delta H_{rxn} = -17$ kcal/mol).

In order to address the question concerning the structure of long-lived, ionized cyclobutanone, and thereby the nature of the hydrogen atom abstraction reaction, the structure of the product ion formed in this reaction was investigated. The product ion must have the structure of protonated cyclobutanone if the reactant ion was cyclic (Scheme I). If the reactant, however, had the γ-distonic structure, an acylium ion would be generated upon hydrogen atom abstraction. The dissociation characteristics of two reference ions, obtained by protonating cyclobutanone and by electron-ionization-induced dissociation of 2-pentanone, were investigated. For comparison, ionized cyclobutanone was generated in cell 1 and reacted with acetone in cell 2, as described above. After this, all unwanted ions were ejected from both cells, and the ions of *m/z* 71 were transferred back to cell 1. These ions were then rapidly accelerated to different, predetermined final kinetic energies and allowed to collide with argon (1×10^{-7} Torr) for 100 ms.[13] The product distribution obtained and the energy dependence of the dissociation reactions, were found to be similar to those measured for the acylium reference ion $CH_3CH_2CH_2C{=}O^+$ and different from those measured for protonated cyclobutanone (Figure 2). These results conclusively show that *the reactive form of ionized cyclobutanone is the acyclic γ-distonic ion.* Furthermore, the hydrogen atom abstraction observed for this ion represents the first reported bimolecular reaction wherein a gaseous radical cation undergoes *bond formation at a radical site remote from the charge site.* This and other radical type reactions of distonic ions, including abstraction of a thiomethyl group from dimethyl disulfide by ionized cyclobutanone, will be discussed in detail in a full manuscript.

Acknowledgment. The support provided to this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is greatly acknowledged.

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(10) For this estimation, the proton affinity of cyclobutanone is assumed to be equal to that of trimethylene oxide (197 kcal/mol). Note: the proton affinities of cyclopentanone and tetrahydrofuran are the same (198.8 kcal/mol); the proton affinity of cyclohexanone differs by less than 1 kcal/mol from that of tetrahydropyran.[11]

(11) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*. (b) Holmes, J. L.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Processes* **1989**, *92*, 111.

(12) The heat of formation of $CH_3CH_2CH_2C{=}O^+$ is estimated to be 134 kcal/mol, assuming that the difference in ΔH_f of $CH_3CH_2C{=}O^+$ ($\Delta H_f = 141$ kcal/mol[11]) and $CH_3CH_2CH_2C{=}O^+$ is similar to that between $CH_3CH_2CH_2CH{=}OH^+$ ($\Delta H_f = 124$ kcal/mol[11]) and $CH_3CH_2CH{=}OH^+$ ($\Delta H_f = 131$ kcal/mol[11]). Use of Benson's group additivity procedure gives 136 kcal/mol.

(13) See, for example: (a) Laude, D. A., Jr.; Johlman, C. L.; Brown, R. S.; Wilkins, C. L. *Mass Spectrom. Rev.* **1986**, *5*, 107. (b) Bensimon, M.; Houriet, R. *Int. J. Mass Spectrom. Ion Processes* **1986**, *72*, 93. (c) Forbes, R. A.; Lech, L. M.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Processes* **1987**, *77*, 107. (d) Katritzky, A. R.; Watson, C. H.; Dega-Szafran, Z.; Eyler, J. *J. Am. Chem. Soc.* **1990**, *112*, 2471–2479. (e) Hop, C. E. C. A.; McMahon, T. B.; Willett, G. D. *Int. J. Mass Spectrom. Ion Processes* **1990**, *101*, 191.

Direct Evidence of the Excited-State Intramolecular Proton Transfer in 5-Hydroxyflavone

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One class of the flavonoids, the flavonols, which comprises 3-hydroxyflavone (3HF) and its related compounds, has been applied as a prototype for studying the dynamics of the proton-transfer reaction in the excited state as well as in the ground state.[1,2] To extend the study of the excited-state intramolecular proton transfer (ESIPT) reaction in flavonoids, we have been investigating many natural plant pigments that may show unusual proton-transfer properties. However, naturally occurring flavonoids have a sugar linkage in the 3-position which precludes the ESIPT reaction. On the other hand, approximately 85% of the flavonoids contain an OH group at the 5-position.[3] A prototype example is 5-hydroxyflavone (5HF), which also possesses an in-

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(1) Barbara, P. F.; Walsh, P. K.; Brus, L. E. *J. Phys. Chem.* **1989**, *93*, 29 and references therein.

(2) Chou, P. T.; Martinez, M. L.; Studer, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 2427 and references therein.

(3) *Naturally Occurring Oxygen Ring Compounds*; Dean, F. M., Ed.; Butterworth & Co.: London 1963; pp 280.

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