

Table I. Kinetic Energy Release in Loss of H₂ from CSH₃⁺

precursor	nominal reaction	T _{0.5} , eV
CH ₃ CH ₂ CH ₂ SH	CH ₂ SH ⁺ → CHS ⁺ + H ₂	0.93
CH ₃ SSCH ₃	CH ₃ S ⁺ → CHS ⁺ + H ₂	0.94
CD ₂ SH	CD ₂ SH ⁺ → CDS ⁺ + HD	0.91
CD ₃ SH	CD ₃ S ⁺ → CDS ⁺ + D ₂	0.93

system one might be able to compare kinetic energy releases for the 1,2-H₂ elimination reaction 1 and the 1,1-H₂ elimination reaction 2 for isomeric ions. Table I records the kinetic energy releases calculated from the half-height widths of the metastable peaks observed¹⁰ for fragmentation of ions nominally of structures CH₂SH⁺ and CH₃S⁺. Both metastable peaks were observed to be "flat-topped" and showed kinetic energy releases identical within experimental error. The mass spectrum of CD₃SH shows⁸ ion currents corresponding, nominally, to CD₃S⁺ and CD₂SH⁺ in the ratio 1:2.2. The former ion showed a metastable peak for loss of D₂, while the latter showed a metastable peak for loss of HD only, the ratio of intensities for the two metastable peaks being the same as the ratio of precursor ion abundances. As shown in Table I, the kinetic energy releases for the two fragmentation reactions are the same and are in agreement with the kinetic energy releases measured for the unlabeled analogues.

Clearly the ions nominally with the thio methoxide structure are not losing H₂ by a simple 1,1-H₂ elimination reaction involving the small kinetic energy release characteristic of 1,1-H₂ elimination reactions.⁵ The identity of the kinetic energy releases suggest an identical reaction pathway for ions with the CH₃S⁺ and CH₂SH⁺ nominal structure. This conclusion can be rationalized in three possible ways. (1) The dissociative ionization of CH₃SR leads not to CH₃S⁺ but rather to CH₂SH⁺ as a result of H migration from carbon to sulfur concurrent with fragmentation.¹¹ (2) The dissociative ionization of CH₃SR and RCH₂SH leads to structurally distinct ions which isomerize to a common structure (or mixture of structures) prior to fragmentation. (3) The CH₃S⁺ and CH₂SH⁺ ions remain structurally distinct but fragment through a common transition state (of energy higher than HCS⁺ + H₂) with the observed kinetic energy release originating from conversion of part of the reverse activation energy into kinetic energy.

The data do not allow a distinction between these possibilities. The available thermochemical data^{8,9} suggest $\Delta H_f(\text{CH}_3\text{S}^+) = 210\text{--}214 \text{ kcal mol}^{-1}$ with $\Delta H_f(\text{CH}_2\text{SH}^+)$ being slightly higher (215–219 kcal mol⁻¹).¹² No reliable experimental value for $\Delta H_f(\text{HCS}^+)$ exists; however, a recent theoretical calculation⁴ gives a value of 245 kcal mol⁻¹ compared with a calculated value of 212 kcal mol⁻¹ for $\Delta H_f(\text{CH}_2\text{SH}^+)$. Thus the fragmentation reactions of both CH₃S⁺ and CH₂SH⁺ are significantly endothermic and metastable ions for fragmentation of both would be expected. The small difference in the heats of formation of the isomeric CSH₃⁺ ions does not permit a clear distinction as to the structure formed by dissociative ionization; at the same time there does not appear to be any energetic driving force for rearrangement during fragmentation of CH₃SR to form CSH₃⁺. With regard to isomerization after fragment ion formation, the MINDO/3 calculations of Dewar and Rzepa⁴ reveal stable bridged structures for CSH₃⁺ which are lower in energy than HCS⁺ + H₂ and could serve as transition states for such an isomerization. However, the observation that the CD₂SH⁺ ion loses only HD (i.e., H/D randomization does not occur) argues against such an isomerization prior to fragmentation. In their MINDO/3 calculations Dewar and Rzepa⁴ have identified a transition state for loss of H₂ from CH₂SH⁺, although they did not report any calculations relating to the CH₃S⁺ structure or the transition state for H₂ loss from this structure. Thus, the

possibility remains that both CH₃S⁺ and CH₂SH⁺ are structurally distinct but fragment through a common transition state, possibly preceded by a bridged intermediate. In any event, the present results are in agreement with the recent conclusions from collisional activation studies¹³ that the fragmentation reactions of nominally isomeric CSH₃⁺ ions are identical for ions of low internal energy.

Work on this and related systems is continuing.

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References and Notes

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- (4) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).
- (5) D. H. Williams and G. Hvistendahl, *J. Am. Chem. Soc.*, **96**, 6755 (1974).
- (6) R. D. Bowen and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 378 (1977).
- (7) Recent results (K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **99**, 366 (1977)) suggest that the reaction is slightly endothermic (3.9 kcal mol⁻¹).
- (8) B. G. Keyes and A. G. Harrison, *J. Am. Chem. Soc.*, **90**, 5671 (1968).
- (9) (a) T. F. Palmer and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 4661 (1962); (b) F. P. Lossing, private communications.
- (10) Observed by the high voltage scanning technique for fragmentation reactions occurring in the first drift region of an A.E.I. MS-902 mass spectrometer operating with a β slit width of 0.008 in. The results in Table I were obtained at 70-eV ionizing energy; however, no electron energy dependence was noted.
- (11) A similar anchimerically assisted process leading to H migration has been proposed for the C₂SH₅⁺ and C₃SH₇⁺ systems: B. van de Graaf and F. W. McLafferty, *J. Am. Chem. Soc.*, **99**, 6806, 6810 (1977).
- (12) However, note that Dill and McLafferty¹³ have concluded that CH₂=SH⁺ is more stable than CH₃S⁺.
- (13) J. D. Dill and F. W. McLafferty, *J. Am. Chem. Soc.*, **100**, 2907 (1978).

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CIDNP Evidence for Electron Transfer between Two Neutral Radicals in Solution¹

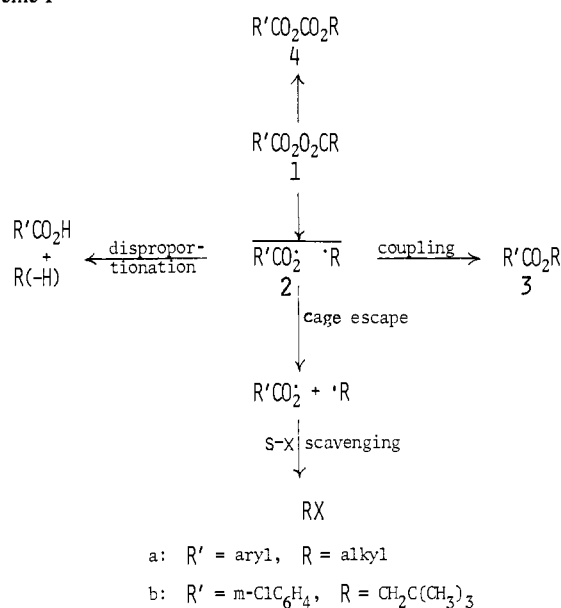
Sir:

It has long been known that mixed diacyl peroxides (**1a**) decompose thermally² by the pathways shown in Scheme I. The polar pathway,^{2,3} which yields a "carboxyl inversion" product⁴ (**4a**), has many of the characteristics of an alkyl-group migration to electron-deficient oxygen.³ The remaining reactions represent collectively the well-known radical pathway for decomposition⁵ in which a pair of radicals (**2**) either recombine or escape from the solvent cage and are scavenged by reaction with the solvent, added scavenger, another molecule of peroxide, or other radicals.

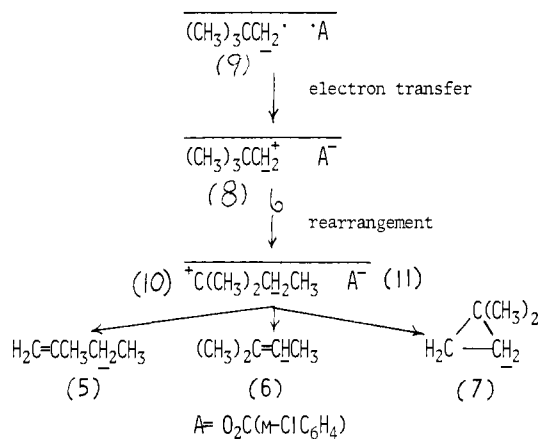
We report here evidence for a previously undocumented electron-transfer pathway for recombination (Scheme II) which competes with radical coupling and disproportionation.⁶ The peroxide employed was *tert*-butylacetyl-*m*-chlorobenzoyl peroxide (**1b**).⁷ In this reaction an electron is transferred between the neopentyl (**9**) and *m*-chlorobenzoyloxy radicals to form *m*-chlorobenzoate (**11**) and the neopentyl cation (**8**). Subsequent Wagner-Meerwein rearrangement of **8** yields cation **10** which loses a proton to produce 2-methyl-1-butene (**5**), 2-methyl-2-butene (**6**), and 1,1-dimethylcyclopropane (**7**) (yields are reported in Table I).

Evidence that products **5–7** arise from the geminate radical pair (**2**) is obtained from the observation of CIDNP during the reaction. In Figure 1 is shown the ¹H NMR spectrum obtained

Scheme I



Scheme II



during the decomposition (half-life 37 s)⁸ of a 0.5 M solution of **1b** in ODCB at 120 °C. CIDNP emission is observed⁹ for the following protons in **5–7**: **5**, methyl CH₂, δ 2.1; **6**, CH, δ 5.2; **7**, CH₂, δ 0.4. The observation of emission for all of these protons is consistent with CIDNP (underlined in Scheme II) generated in the α protons of **9** in a radical pair with *m*-chlorobenzoyloxy radical.¹⁰ Furthermore, the vinyl protons of **5** (δ 4.7) are, as predicted, not polarized. The polarization developed in **9** is then transferred to **5–7** by subsequent rapid electron-transfer and rearrangement reactions. The remaining polarized signals in Figure 1 are from the products typically obtained from thermally decomposing peroxides, including neopentane (**12**) formed by the scavenging of neopentyl radicals.^{10,11} When hexachloroacetone (HCA) is used as solvent the CIDNP spectrum is similar except for the addition of a strongly enhanced absorption signal due to neopentyl chloride which replaces **12** as the product of scavenging.

Previous investigations of neopentyl and related radicals¹² indicate that they rearrange far too slowly (if at all)¹³ to be a direct precursor of **5–7**. The rapid rearrangement of cation **8**, on the other hand, is supported by the observation¹⁴ that solvolysis of neopentyl tosylate in aqueous ethanol at 120 °C produces **5–7** in relative yields of 49.7, 49.7, and 0.56%, respectively, presumably via the intermediate **8**. The fact that these product ratios differ somewhat from those obtained from **1b** probably reflects differences in the medium and cation precursor in the two cases.¹⁵

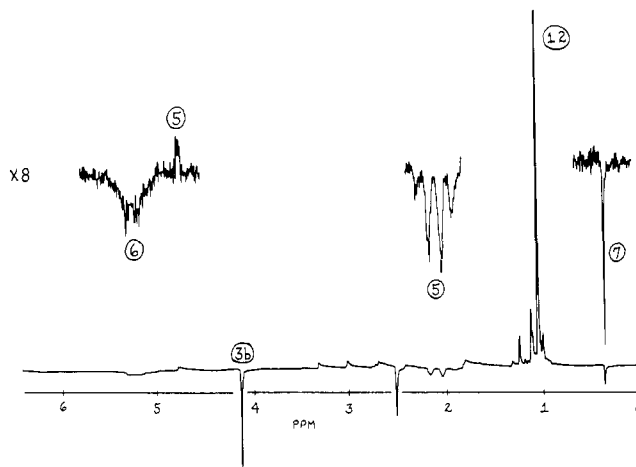


Figure 1. 60-MHz ¹H NMR spectrum recorded during the thermolysis of **1b** (0.5 M) in ODCB at 120 °C. The spectrum is an average of 9 scans, collected with a 15° rf pulse angle and a repetition rate of 1 scan every 5 s. Collection began 90 s after the sample was placed in a preheated NMR probe. Numbers refer to compounds discussed in the text.

Table I. Product Yields from Thermolysis^a of **1b**

product	yield, %
ArCO ₂ CH ₂ CMe ₃ (3b)	14.8 ± 1.4 ^b
2-methyl-1-butene (5)	26.7 ± 4.0 ^b
2-methyl-2-butene (6)	3.8 ± 0.6 ^c
1,1-dimethylcyclopropane (7)	0.66 ± 0.08 ^c
neopentane (12)	9.4 ± 3.0 ^b (11.2 ± 2.1) ^c
ArCO ₂ CO ₂ CH ₂ CMe ₃ (4b)	17.9 ± 1.6 ^b

^a 0.5 M, *o*-dichlorobenzene, 120 °C. ^b NMR integration relative to **1b**. ^c GC assuming yield of **5** to be that determined by NMR.

It seems likely that the electron-transfer process described here is a general phenomenon occurring whenever two radicals with much different electronegativities encounter each other.¹⁶ If so, it presents an intriguing opportunity for producing ion pairs in media of low dielectric constant. Furthermore, two other reports have recently appeared¹⁷ of carbon skeleton rearrangements in mixed peroxides which also exhibit CIDNP. In these cases, however, it was concluded that the CIDNP and rearrangement were not related sequentially. Our results suggest that a reexamination of these and other radical-pair reactions for evidence of electron transfer may be in order.

Acknowledgments. Financial support from the National Science Foundation is gratefully acknowledged. We also thank Professors J. E. Leffler and T. H. Morton for helpful discussions.

References and Notes

- (1) A preliminary report of this work was presented at the 7th Northeast Regional Meeting of the American Chemical Society, Albany, N.Y., Aug 8–11, 1976.
- (2) For a recent review, see R. Hiatt in "Organic Peroxides", Vol. 2, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, p 799.
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- (4) It has also been reported^{9b} that **4a** may decompose to give **3a**.
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- (7) **1b** was synthesized in 80% yield from *m*-chloroperbenzoic acid and *tert*-butylacetyl chloride: M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, **63**, 526 (1941).
- (8) The half-life was calculated from the first-order rate constant for disappearance of the methyl resonance in the NMR spectrum of **1b** during heating.
- (9) Assignments were made by comparison of the CIDNP spectrum with

- spectra of authentic samples of the products taken in sealed tubes at 120 °C.
- (10) For an application of the qualitative rules for CIDNP to the decomposition of a closely related peroxide, see R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Am. Chem. Soc.*, **94**, 552 (1972).
 - (11) The carboxyl inversion product (**4b**) is formed in 18% yield but does not exhibit CIDNP in either the ¹H or ¹³C NMR. This supports a nonradical mechanism for formation of this product. Furthermore, **4b** is stable under the reaction conditions and is thus not a precursor of **3b** or **5-7**. The relative yields of **3b** and **5-7** are also insensitive to the concentration of **1b** (0.045–0.5 M) and to the addition of excess *m*-chlorobenzoic acid (saturated in ODCB at 0.2 M). This makes it unlikely that either induced decomposition or acid promoted ionization of **1b** contribute significantly to the reaction under these conditions.
 - (12) (a) J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, p 333; (b) E. J. Hamilton and H. Fischer, *Helv. Chim. Acta*, **56**, 795 (1973); (c) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).
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 - (14) G. M. Fraser and H. M. R. Hoffman, *Chem. Commun.*, 561 (1967).
 - (15) The predominance of the less substituted olefin, **5**, suggests that the ion pairs formed from the peroxide resemble those formed in the gas phase: W. J. Marinelli and T. H. Morton, *J. Am. Chem. Soc.*, **100**, 3536 (1978); J. Bullivant, J. S. Shapiro, and E. S. Swinbourne, *ibid.*, **91**, 7703 (1960). The intermediacy of *tert*-butylcarbene, formed by hydrogen abstraction from the neopentyl radical, would be expected to yield a much higher proportion of dimethylcyclopropane than observed: W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, p 238.
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 - (17) K. G. Taylor and M. Kaelin, Abstract of Papers, the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 20–Sept 3, 1976; P. B. Shevlin and H. J. Hansen, *J. Org. Chem.*, **42**, 3011 (1977).

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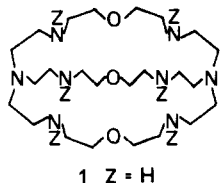
Molecular Recognition. Anion Cryptates of a Macrobicyclic Receptor Molecule for Linear Triatomic Species

Sir:

Macropolycyclic molecules provide a particularly attractive entry into the organization of space required by the design of *nonbiological molecular receptors* endowed with high recognition toward a substrate of defined geometric and electronic properties.¹

Spheroidal cavities lined with donor binding sites display spherical recognition; they form highly stable and selective inclusion complexes with spherical cations, the alkaline and alkaline-earth *cation cryptates* of macrobicyclic and macrotricyclic ligands.¹⁻³ Inversion of the properties of the nitrogen binding sites of spherical macrotricycles³ by protonation leads to highly stable and selective *anion cryptates* of the spherical halide anions.⁴⁻⁶

We now report the properties of a macrobicyclic receptor molecule **1** designed for the *recognition of linear triatomic*



species XYZ. The results obtained add a further step to an emerging new field of coordination chemistry: anion complexes or organic ligands.⁴⁻⁹

The synthesis of the bis-tren macrobicyclic **1** has been described earlier; it forms binuclear cryptates by inclusion of two

transition metal cations, each held by a tren subunit at the poles of the ellipsoidal cavity.¹⁰ Protonation of **1** in aqueous solution shows the successive fixation of six protons with the following pK's: 9.3, 9.0, 7.9, 7.4, 6.3, and 5.7 ± 0.1 (at 25 °C). The remaining two nitrogens are much more difficult to protonate (pK < 3.0); tren itself forms a triprotonated species N(CH₂CH₂NH₃⁺)₃.^{11,12} Similarly, in the hexaprotonated bis-tren molecule (**1-H₆⁶⁺**), protonation is expected to occur at the six secondary nitrogen sites in the bridges. Highly crystalline hexasalts (**1-H₆⁶⁺**)₆X⁻ (X⁻ = Cl⁻, ClO₄⁻) are obtained from methanol-water (M/W) solutions of **1** containing 6 equiv of acid.

(**1-H₆⁶⁺**) provides an ellipsoidal cavity with inverted binding sites as compared to **1** itself: three positively charged ammonium groups are located around the molecular axis at each pole of the cavity, providing sites for binding of electron-rich substrates of compatible size via ionic hydrogen bonds.

Crystalline solids are obtained from M/W solutions of the hexaperchlorate or hexanitrate of **1** containing 1 equiv of sodium azide. Analytical data indicate that they are monoazide species (**1-H₆⁶⁺**)N₃⁻·5X⁻ (X⁻ = ClO₄⁻, NO₃⁻). The infrared spectrum of the perchlorate species (in nitromethane) displays a strong band at 2085 ± 5 cm⁻¹ for the asymmetric stretching vibration of N₃⁻.¹³ It is markedly shifted from the corresponding band of unbound N₃⁻ (2052 ± 5 cm⁻¹) when excess NaN₃ is added, in the same direction as observed when N₃⁻ is bound to carbonic anhydrase (2094 cm⁻¹).¹⁴ Similarly in the presence of excess (>1 equiv) NaN₃, the Raman spectrum (aqueous solution at pH 5) shows a well-resolved doublet for the symmetrical stretching mode at 1363 ± 1 and 1343 ± 1 cm⁻¹ for complexed and free N₃⁻, respectively.¹⁵

The 250-MHz ¹H NMR spectrum of (**1-H₆⁶⁺**)₆ClO₄⁻ (in CD₃NO₂ at 24 °C) shows broadened resonances at 3.05, 3.55, and 4.00 ppm (from Me₄Si) with relative intensities of 1, 2, and 1, respectively due to CH₂N, CH₂N⁺, and CH₂O protons, confirming the hexaprotonated nature of the ligand. Addition of 1 equiv of NaN₃ gives a spectrum containing four signals of same areas at 3.0, 3.45, 3.53, and 4.03 ppm; when only 0.5 equiv of NaN₃ is added a superposition of these two spectra is obtained with additional line broadening. The azide-containing species retains the threefold symmetry of the ligand molecule: the three bridges of the macrobicyclic are equivalent; this cannot be due to exchange averaging since the **1-H₆⁶⁺** and the azide species are in slow exchange on the NMR time scale at 24 °C, as shown by the spectrum obtained at 0.5 equiv of NaN₃.

From the analytical and spectral results one may infer that the azide species is a complex of 1:1 stoichiometry and of threefold symmetry (on the NMR time scale). This agrees with its formulation as the *anion cryptate* [N₃⁻·(**1-H₆⁶⁺**)] resulting from inclusion of the azide anion into the ellipsoidal intramolecular cavity of the hexaprotonated ligand. The electronic and geometric features of the azide anion are complementary to those of the receptor molecule (**1-H₆⁶⁺**): N₃⁻ has negative charge and high electron density with cylindrical distribution at both ends;¹⁶ its size is such that it may tightly fit into the cavity and form hydrogen bonds simultaneously to the secondary ammonium sites at both poles.¹⁷ An azide cryptate structure like **2** would agree with these considerations:

