

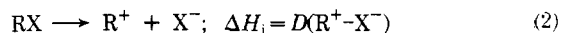
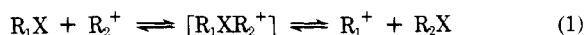
Communications to the Editor

Relative Stabilities of Carbonium Ions in the Gas Phase and Solution. A Comparison of Cyclic and Acyclic Alkylcarbonium Ions, Acyl Cations, and Cyclic Halonium Ions

Sir:

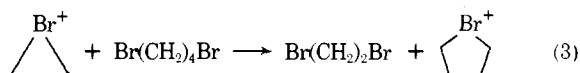
A thorough and fundamental understanding of chemical transformations in solution demands an assessment of solvent effects on ion stabilities. Ionic heats of solvation can be determined by combining gas phase and solution data in appropriate thermochemical cycles. Such studies have been carried out for protonation of amines in aqueous solution,¹⁻³ protonation of amines and phosphines in fluorosulfuric acid (HSO₃F),⁴⁻⁶ and deprotonation of alcohols in dimethyl sulfoxide.^{5,7}

Recently we described ion cyclotron resonance techniques⁸⁻¹⁰ which permit determination of carbonium ion stabilities by examining the preferred direction and equilibrium in reaction 1, where the relative binding energy of the reference base X⁻ to two carbonium ions (Lewis acids) is




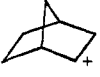
determined. Carbonium ion stabilities can thus be assessed by comparing their R-X heterolytic bond dissociation energies as defined by eq 2 ($\Delta H_i \equiv$ bromide affinity when X⁻ = Br⁻). We wish to report preliminary data for the relative stabilities, using the reference base Br⁻, of a series of ions R⁺, including cyclic and acyclic alkylcarbonium ions, acyl cations, and cyclic bromonium ions. These data are of particular interest since heats of ionization in fluorosulfuric acid are available for several of the bromides.¹¹⁻¹³ Combined with these data our results yield interesting insights into the effect of solvation on relative carbonium ion stabilities.

Experiments were performed as previously described for the reference base F⁻.¹⁰ Data for two systems of interest are shown in Figure 1. In a mixture of 1,2-dibromoethane and 1,4-dibromobutane, reaction 3 is observed to proceed entirely to the right (Figure 1a). In reaction 4, 1-adamantyl

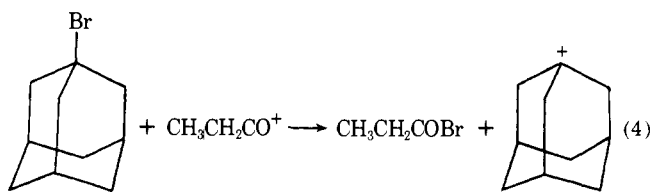


bromide is observed to transfer Br⁻ to CH₃CH₂CO⁺ (Figure 1b). For a series of carbonium ions R⁺, similar experi-

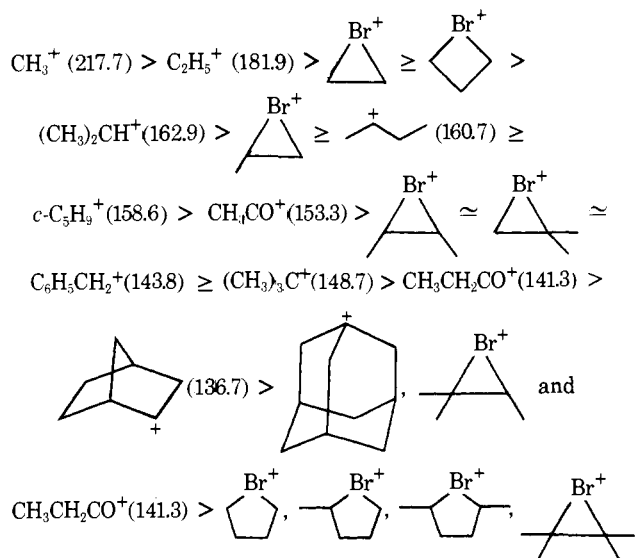
Table I. Estimated Relative Enthalpies of Solution of R⁺ in HSO₃F^a

R ⁺	ΔH_i^b (g)	ΔH_i^c (s)	$\Delta H_s^{d,e}$ (R ⁺ + Br ⁻)	$\delta_R \Delta H_s^g$ (R ⁺)
CH ₃ CO ⁺	153.3 ± 1	-29.8 ± 3	-190.1 ± 3	-20
Br ⁺ \triangle	169.9 ± 7	+1.0	-178.6 ± 8	-8
CH ₃ CH ₂ CO ⁺	141.3 ± 3	-28.0 ± 5	-177.6 ± 6	-7
Br ⁺ \triangle	159.2 ± 1	-3.3 ± 0.5	-172.2 ± 1	-2
(CH ₃) ₃ C ⁺	148.7 ± 1	-14.5 ± 2	-170.5 ± 2	0
Br ⁺ \triangle	146.8 ± 2	-8.4 ± 0.9	-165.8 ± 2	5
	<137.5	-14.3 ± 0.2	>-166.3 ^f	>4
Br ⁺ \square	<136.0	-13.8 ± 1.9	>-162.5	>8
	138.5 ± 2	-13 ^h	-160.3 ± 3	10 ^h
Br ⁺ \triangle	<134.6	-13.4 ± 0.9	>-159.8	>11

^a All data in kcal/mol at 298 K. ^b Gas phase bromide affinities $D(R^+-Br^-)$ were determined by combining experimental results for bromide transfer reactions with calculated values for reference compounds; corrections were made for entropy terms arising from symmetry numbers, ring closure, and mixing (see text). ^c Heats of ionization for RBr in HSO₃F are from ref 11-13, 22, 23. ^d Heats of solvation for R⁺ + Br⁻ in HSO₃F were calculated *via* a thermochemical cycle similar to that described in ref 1. ^e Heats of vaporization used in the cycle are from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970, or were estimated from boiling point data. ^f The heat of sublimation of adamantyl bromide (a solid at room temperature) used in the cycle was estimated using data from P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970), as described in A. Bondi, *J. Chem. Eng. Data*, **8**, 371 (1963). ^g Heats of solvation of R⁺ relative to that of (CH₃)₃C⁺. ^h See footnote 23.



ments indicate the following order for relative *free energies* of RBr heterolytic bond cleavage:¹⁴



Estimates of bromide affinities, $D(\text{R}^+-\text{Br}^-)$, from available thermochemical data are given in parentheses in kilocalories per mole.¹⁵⁻²⁰ The enthalpies of bromide transfer can be estimated from the relative free energies by making the appropriate corrections for entropy changes. It is expected that with the exception of symmetry number changes, ΔS will be small for processes such as reaction 4 but cannot be ignored in processes such as reaction 3 where entropies of cyclization are large. Estimates of this effect indicate that the bromide affinities for the three-, four-, and five-membered ring bromonium ions would respectively decrease by 2.9, 3.6, and 4.3 kcal/mol relative to the alkyl carbonium ions and acyl cations in the above series.²¹

Determination of heats of ionization in HSO_3F at -60° yield the following heterolytic bond energies in solution (in kcal/mol)^{11-13,22,23}

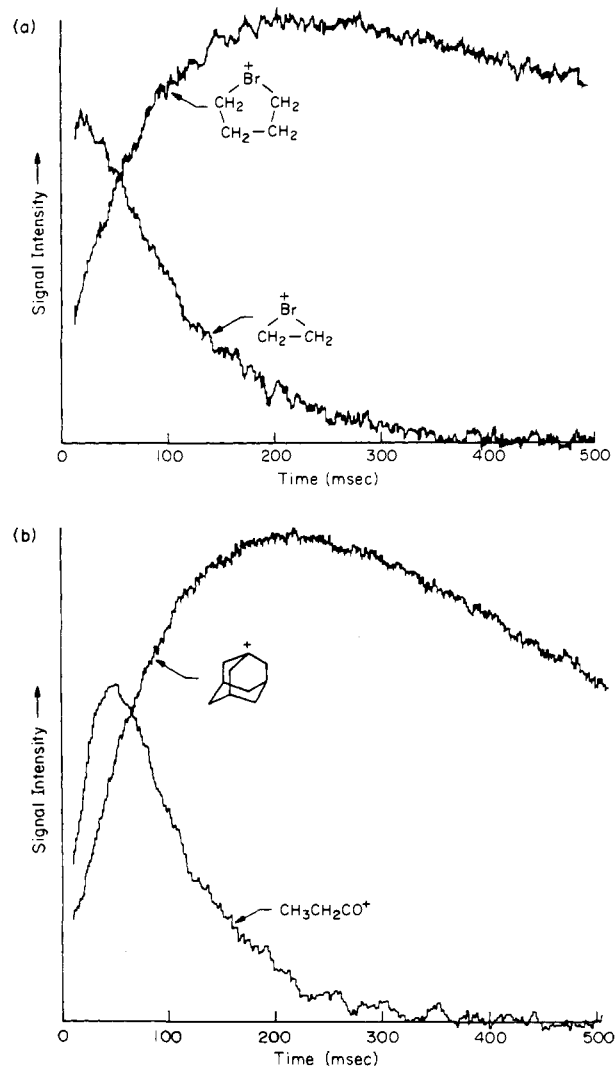
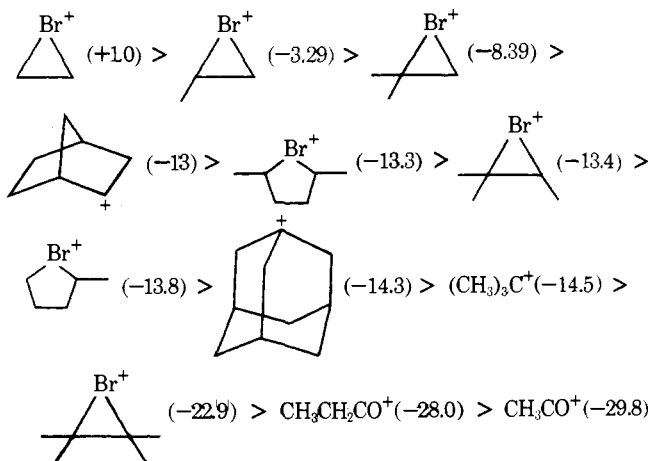


Figure 1. Variation of ion abundance with time in two mixtures of bromides. Relative carbonium ion stabilities in the gas phase with respect to Br^- are determined from the direction of Br^- transfer: (a) 6:1 mixture of 1,4-dibromobutane and 1,2-dibromoethane at a total pressure of 2×10^{-6} Torr, tetramethylene bromonium ion is more stable than ethylene bromonium ion (reaction 3); (b) 1:1 mixture of adamantyl bromide and propionyl bromide at a total pressure of 2×10^{-6} Torr, adamantyl cation is more stable than propionyl cation (reaction 4). Buildup of the displayed species during the first 50 msec is due in part to reaction by fragment ions (not shown) following the initial 10 msec, 16 eV electron beam pulse.

Using bromide affinities as a measure of carbonium ion stability, the following conclusions emerge from analysis and comparison of these data.

(1) Although solvent has an appreciable effect in attenuating the observed range, the relative bromide affinities of cyclic bromonium ions are the same in the gas phase and in solution. Stability increases with increasing ring size and, in the three-membered rings, methyl substitution.

(2) Relative to acyclic alkyl carbonium ions and acyl cations, cyclic bromonium ions are significantly more stable in the gas phase than in solution. Cyclic bromonium ions can be regarded as internally solvated carbonium ions in the gas phase.

(3) While of comparable stability in solution, the 1-adamantyl carbonium ion is significantly more stable than the *tert*-butyl carbonium ion in the gas phase, possibly by as much as 11 kcal/mol. This indicates that the strain energy due to the nonplanarity of the carbonium ion center²⁴ in the 1-adamantyl carbonium ion relative to the *tert*-butyl carbo-

nium ion is smaller than the stabilization afforded by the interaction of the charge with the polarizable hydrocarbon framework. Again, the ion is internally solvated in the gas phase.

(4) The above results permit semiquantitative estimates of relative enthalpies of solvation for carbonium ions in HSO_3F . Relevant data for several ions are summarized in Table I.

Acknowledgment. This research was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3)767-8. The ion cyclotron resonance spectrometer used in these studies was financed by the National Science Foundation under Grant No. NSF-GP-18393. We would also like to thank Professor P. v. R. Schleyer for providing the 1-adamantyl bromide used in this study.

References and Notes

- (1) E. M. Arnett, F. M. Jones, III, J. Taagepera, W. H. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).
- (2) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).
- (3) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).
- (4) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973).
- (5) E. M. Arnett, *Accounts Chem. Res.*, **6**, 404 (1973).
- (6) R. H. Staley and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **96**, 6252 (1974).
- (7) E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph, and R. P. Quirk, *J. Amer. Chem. Soc.*, **95**, 1492 (1973); E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *ibid.*, **96**, 5640 (1974).
- (8) For a general review see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
- (9) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 8934 (1972).
- (10) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **96**, 1269 (1974).
- (11) J. W. Larsen and A. V. Metzner, *J. Amer. Chem. Soc.*, **94**, 1614 (1972).
- (12) E. M. Arnett, J. W. Larsen, and J. V. Carter, private communication.
- (13) G. A. Olah and T. R. Hockswender, Jr., *J. Amer. Chem. Soc.*, **96**, 3574 (1974).
- (14) In the ordering given $>$ indicates that the reaction proceeds entirely to the right, \geq indicates that the reaction proceeds preferentially to the right but also in the reverse direction as indicated by double resonance experiments, and a comma indicates that the relative order could not be definitely determined either because the Br^- transfer reaction was too slow to reach a definite conclusion or because (as in the case of *tert*-butyl and propionyl) the ions have the same mass. The rate constant for Br^- transfer reactions involving the five-membered bromonium ions decreased markedly with increasing methyl substitution.
- (15) Neutral heats of formation $\Delta H_f^\circ(\text{RBr})$ are from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970, or were estimated using group heats as described by S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968.
- (16) Ionic heats of formation for C_5H_9^+ and $\text{CH}_3\text{CH}_2\text{CO}^+$ are from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U.S. Government Printing Office, Washington, D. C., 1969.
- (17) The heat of formation of CH_3CO^+ is from D. Reinke, R. Krabig, and H. Baumgartel, *Z. Naturforsch. A*, **28**, 1021 (1973).
- (18) The heat of formation of norbornyl cation is based on a determination of the proton affinity of norbornene (F. Kaplan, P. Cross, and R. Prinstein, *J. Amer. Chem. Soc.*, **92**, 1445 (1970)) revised to reflect more recent values for the reference compounds (R. H. Staley and J. L. Beauchamp, unpublished results; R. W. Taft, private communication).
- (19) Other ionic heats of formation are from F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970); F. P. Lossing, *ibid.*, **49**, 357 (1971); W. Tsang, *J. Phys. Chem.*, **76**, 143 (1972).
- (20) $\Delta H_f^\circ(\text{Br}^-) = -52.3$ kcal/mol is used based on values for $\Delta H_f^\circ(\text{Br})$ from D. R. Stoll and H. Prophet, "JANAF Thermochemical Tables," 2nd ed, NSRDS-HBS 37, U.S. Government Printing Office, Washington, D.C., 1971, and for $\text{EA}(\text{Br})$ from R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).
- (21) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N.Y., 1968, p 51 ff.
- (22) Heats of ionization of CH_3COBr and $\text{CH}_3\text{CH}_2\text{COBr}$ were calculated from data for the acid chlorides, J. W. Larsen, P. A. Bouis, M. W. Grant, and C. A. Lane, *J. Amer. Chem. Soc.*, **93**, 2067 (1971).
- (23) Recent experiments suggest that the heat of ionization of norbornyl bromide in solution relative to *tert*-butyl bromide may be somewhat reduced (E. M. Arnett, private communication). This would also reduce the heat of solvation of the norbornyl cation relative to $(\text{CH}_3)_3\text{C}^+$ (Table I).
- (24) Relative strain energies of *tert*-butyl and 1-adamantyl carbonium ions are discussed in G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(25) National Science Foundation Undergraduate Research Program participant, Summer, 1974.

(26) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.

Robert D. Wieting,²⁵ Ralph H. Staley, J. L. Beauchamp*²⁶

Contribution No. 4934, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology Pasadena, California 91125

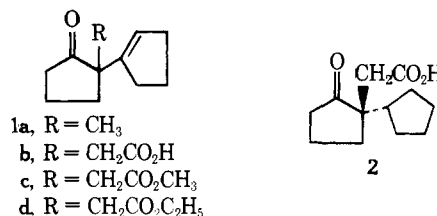
Received July 29, 1974

Stereospecificity in Triplet State Photorearrangements. The Oxa-di- π -methane Photorearrangement.¹ Mechanistic Studies in Photochemistry²

Sir:

Photorearrangements of β,γ -unsaturated ketones have been characterized as either 1,3-acyl migrations or oxa-di- π -methane rearrangements.³ A number of studies have shown that the former occurs by an excited singlet $\pi 2_s + \sigma 2_s$ migration (or its equivalent).⁴ The oxa-di- π -methane rearrangement has also been established as an excited state triplet reaction.⁵ However, the stereochemical consequences of this reaction have not been fully characterized. Several studies have appeared which purport to determine the stereochemical results but the conclusions are contradictory, in one case suggesting a $\pi 2_s + \sigma 2_s$ pathway⁶ while other reports suggest a $\pi 2_a + \sigma 2_a$ rearrangement.⁷ These studies have been carried out on β,γ -unsaturated ketones in which secondary factors (*e.g.*, steric hindrance) may exert a significant or perhaps controlling influence on the course of the rearrangement.

In order to minimize secondary factors and to assure the occurrence of an oxa-di- π -methane rearrangement, we have constructed the model system, 2-(1-cyclopentenyl)-2-methylcyclopentanone (**1a**) and its derivatives,⁸ in order to test the stereochemical consequences at carbon-2 (C-2).⁹ The photorearrangements of **1** under direct or acetone-sensitized conditions are unexceptional and isolated product yields are very good,¹⁰ permitting a thorough mechanistic investigation.



The keto acid **1b** was resolved as the cinchonidine salt into its optical antipodes, and the configurations of the derived carboxylic acids were assigned as (*S*)-**1b** ($[\alpha]^{28\text{D}} + 139^\circ$) and (*R*)-**1b** ($[\alpha]^{28\text{D}} - 138^\circ$) by correlation of the Cotton effects of their CD spectra with the modified octant rule for β,γ -unsaturated ketones¹¹ and the application of the octant rule for the Cotton effect of the saturated derivative (**2**), the carbon-carbon double bond reduction product of (*R*)-**1b** (Table I). Greater than 90% optical purities of the individual enantiomers were demonstrated by use of the chiral shift reagent, *tris*(3-heptafluoropropylhydroxymethylene-*d*-camphorato)europium(III)¹² with the derived methyl esters (**1c**).

Examination of the direct irradiation product of each of the enantiomeric acids confirmed that a stereospecific 1,3-acyl migration occurred consistent with a 1,3-sigmatropic ($\pi 2_s + \sigma 2_s$) mechanism.⁴ The optical purities of the products