obtained by increasing the concentration of aniline and/or Dabco until complete conversion resulted. The previously reported value[19] of ϵ 30 400 M^{-1} cm^{-1} at λ_{max} 446 nm was confirmed.

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Carbenium Ion Stabilities in the Gas Phase and Solution. An Ion Cyclotron Resonance Study of Bromide Transfer Reactions Involving Alkali Ions, Alkyl Carbenium Ions, Acyl Cations, and Cyclic Halonium Ions

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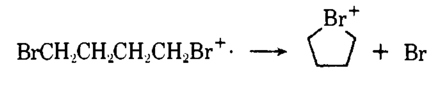
Abstract: Ion cyclotron resonance techniques are used to measure relative heterolytic bond dissociation energies $D(R^+\text{-}Br^-)$ in the gas phase for a series of alkali cations, alkyl carbenium ions, acyl cations, and cyclic halonium ions. $D(R^+\text{-}Br^-)$ for adamantyl cation is found to be less than for *tert*-butyl cation. A proton affinity for norbornene of $D(B\text{-}H^+) = 198.8 \pm 2$ kcal/mol is determined from which $D(R^+\text{-}Br^-) = 146.8 \pm 2.3$ kcal/mol is calculated for norbornyl cation, 16 kcal/mol less than for cyclopentyl cation. In several cases additional thermochemical data useful in assessing absolute $D(R^+\text{-}Br^-)$ heterolytic bond dissociation energies are provided by photoionization mass spectrometry. Relative enthalpies of solvation for carbenium ions are estimated via appropriate thermochemical cycles by combining the gas phase data with heats of ionization in a HSO_3F/SbF_5 medium. The results show that solvation enthalpies are related to ion size with smaller ions being better solvated. Relative stabilities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and in the three-membered rings with methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

The quantitative assessment of the energetics of carbenium ion formation and solvation is a difficult problem in organic chemistry. Relatively few stable carbenium ions have been thoroughly studied in aqueous media, where more often these species are invoked as transient intermediates in a wide range of chemical transformations.[2] Only recently has it been possible to devise conditions compatible with the existence of these reactive species for periods of time which permit their study using a variety of spectroscopic techniques.[3-6] With the assurance based on NMR and other spectral data that solution of selected halide precursors in magic acid (HSO_3F containing ca. 11% SbF_5) leads exclusively to ions of the anticipated structures,[6] calorimetric studies have been carried out leading to the determination of heats of ionization in these solvent systems.[7,8]

In the gas phase carbenium ions are readily produced by electron impact (EI) ionization of halide precursors, process 1.[9] In the case of dihalides, internal displacement in the parent cation, for example, process 2, leads to the production of cyclic halonium ions.[9-11] This is analogous to reaction 3 in which alkyl halide parent ions react with neutral alkyl halides to give dialkylhalonium ions.[12]

$$RX \xrightarrow{EI} [RX^{+}\cdot]^{*} + e^{-} \rightarrow R^{+} + X\cdot + e^{-} \qquad (1)$$



(2)

$$RX^{+}\cdot + RX \rightarrow RXR^{+} + X\cdot \qquad (3)$$

Ion cyclotron resonance (ICR) techniques, which have been previously described for the reference base F^-, permit the determination of relative gas phase carbenium ion stabilities by examining the preferred direction and equilibrium in reaction 4.[13-15] The reaction proceeds through an intermediate halonium ion complex which is more stable than either reactants or products.[12] The heterolytic bond dissociation energy $D(R^+\text{-}X^-)$ as defined by eq 5 [$D(R^+\text{-}X^-) \equiv$ halide affinity] is taken as a measure of gas phase stability of R^+.

$$R_1^{+} + R_2X \rightleftharpoons [R_1XR_2^{+}]^{*} \rightleftharpoons R_1X + R_2^{+} \qquad (4)$$

$$RX \rightarrow R^{+} + X^{-}, \Delta H = D(R^{+}\text{-}X^{-}) \qquad (5)$$

Alkali cations are also readily produced in the gas phase, by emission from thermionic sources, and may be studied by ICR techniques to provide additional species for the comparison of relative stabilities using reaction 4, R = Li^+, Na^+, and K^+.[16,17]

The present work reports ICR studies of the relative gas phase stabilities with respect to the reference base Br^- of a series of ions R^+ including alkali ions, alkyl carbenium ions, acyl cations, and cyclic halonium ions, and the assessment of the solvation energetics of these ions in fluorosulfuric acid media based on the comparison of the gas phase and solution results.[18] Additional reference data useful in assessing absolute $D(R^+\text{-}Br^-)$ heterolytic bond dissociation energies are developed using photoionization mass spectrometry.

Experimental Section

ICR instrumentation and techniques used in these studies have been previously described in detail.[12-14,16-20] Two instruments were employed, with all of the alkali ion results being obtained using a standard Varian V5900 ion cyclotron resonance mass spectrometer equipped with a 9-in. magnet system. Other studies utilized an instrument built in the shops at Caltech which incorporates a 15-in. magnet system and is similar in other respects to the Varian spectrometer.

Alkali ions were generated by a thermionic source which was mounted on the trapping electrode inside the source region of the ICR cell, next to the electron emission source. The thermionic source consists of a small (<1 mm diameter) glass bead containing equal parts of an alkali oxide, SiO_2, and Al_2O_3, on a 7-mil rhenium filament wire.[20] By appropriately biasing the emitter it is possible to confine alkali ions in the trapping well. While the spectrometer was operated in the drift mode for the studies reported herein, we have successfully performed trapped ion experiments by pulsing the bias applied to the thermionic emitter to fill the trapping region with alkali ions at the start of the trapping sequence.[17]

The photoionization mass spectrometer used in these studies is described in detail elsewhere.[21] Photoionization efficiency curves were recorded at ambient temperature (296 K) with a resolution of 1 Å.

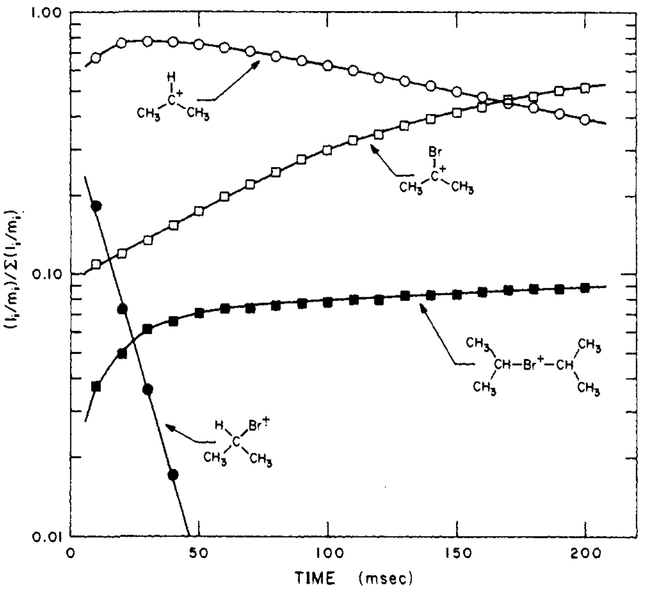


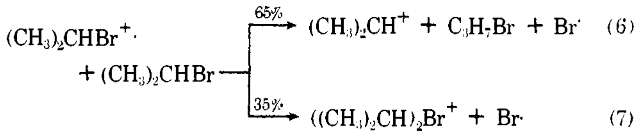
Figure 1. Variation of ion abundance with time following a 10 ms, 12.0 eV electron beam pulse in $(CH_3)_2CHBr$ at 2×10^{-6} Torr: ●, $(CH_3)_2CHBr^{+}\cdot$; ○, $(CH_3)_2CH^+$; □, $(CH_3)_2CBr^+$; ■ $((CH_3)_2CH)_2Br^+$.

$(CD_3)_2CHBr$ was prepared by reduction of $(CD_3)_2CO$ to $(CD_3)_2CHOH$ using $LiAlH_4$ in bis(2-ethoxyethyl) ether followed by distillation; $(CD_3)_2CHOH$ was then reacted with PBr_3 at −10 °C to give $(CD_3)_2CHBr$ which was purified by distillation. 2,3-Dibromo-2-methylbutane and 2,3-dibromo-2,3-dimethylbutane were synthesized by the bromination of the appropriate olefin in CH_2Cl_2 at −10 °C. 1-Adamantyl bromide was kindly provided by Professor P. v. R. Schleyer. Other chemicals were obtained from commercial sources. Samples were examined by mass spectrometric analysis to determine purities; several compounds were further purified by distillation. All samples were degassed at liquid nitrogen temperature before use. ICR experiments were performed at ambient temperature (~296 K).

Results

The gas phase ion chemistry of each of the organic bromides, RBr, used in the study of relative stabilities was briefly investigated by examining the variation of ion abundance with pressure and with time and by double resonance experiments.[12-14] The major ion in the mass spectra of these molecules, even at low electron energies, is the fragment R^+.[9-13] While in several systems slow hydride abstraction or condensation reactions with the parent neutral were observed, in mixtures with other neutral bromides, bromide transfer, reaction 4, is fast, allowing the preferred direction of this reaction to be readily ascertained.[12,13,18]

Monobromides. The ion chemistry of isopropyl bromide was examined in detail and found to be similar to that of methyl and ethyl bromide which has been previously reported.[12] At 12.0 eV the only species present in the mass spectrum of $(CH_3)_2CHBr$ are the parent ion, $(CH_3)_2CHBr^{+}\cdot$ (*m/e* 122 and 124) and the isopropyl cation, $(CH_3)_2CH^+$ (*m/e* 43). Variation of ion abundance with time following a 10-ms, 12.0-eV electron beam pulse is shown in Figure 1. The parent ion reacts to give the isopropyl cation, reaction 6, and diisopropylbromonium ion, reaction 7, with an overall rate constant of 8×10^{-10} cm^3 molecule^{-1} s^{-1}. Hydride abstraction by the isopropyl cation, reaction 8, proceeds with a rate constant of 0.7×10^{-10} cm^3



$$(CH_3)_2CHBr^{+}\cdot + (CH_3)_2CHBr \xrightarrow{65\%} (CH_3)_2CH^{+} + C_3H_7Br + Br\cdot \qquad (6)$$

$$(CH_3)_2CHBr^{+}\cdot + (CH_3)_2CHBr \xrightarrow{35\%} ((CH_3)_2CH)_2Br^{+} + Br\cdot \qquad (7)$$

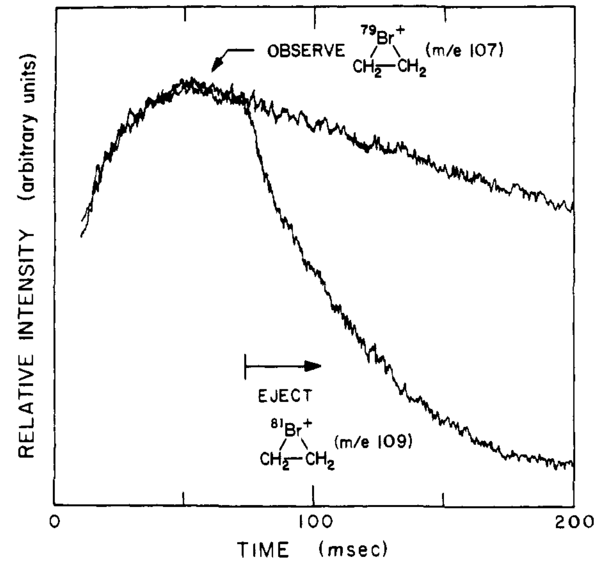


Figure 2. Variation of ion intensity with time following a 10 ms, 16.0 eV electron beam pulse in $BrCH_2CH_2Br$ at 4.0×10^{-6} Torr for $C_2H_4{}^{79}Br^+$ (*m/e* 107) with and without continuous ejection of $C_2H_4{}^{81}Br^+$ (*m/e* 109) starting at 75 ms. From the observed first-order decay, a rate constant of 1.3×10^{-10} cm^3 molecule^{-1} s^{-1} is obtained for reaction 16.

molecule^{-1} s^{-1}. The product $C_3H_6Br^+$ (*m/e* 121 and 123) is not observed to undergo further reaction. At higher pressures the isopropyl cation clusters to form the diisopropylbromonium ion, reaction 9. This accounts for the slow increase of $((CH_3)_2CH)_2Br^+$ abundance at long times in Figure 1. In order to identify the site of hydride abstraction in reaction 8, ion-molecule reactions in $(CD_3)_2CHBr$ were examined. Ion abundance and double resonance results indicate that of the two possible reactions 10 and 11, only the former occurs, indicating that hydride loss involves exclusively the secondary position. Studies of a mixture of $(CH_3)_2CHBr$ and $(CD_3)_2CHBr$ were consistent with the previously proposed mechanism for hydride transfer involving participation of a symmetric dialkylhalonium ion intermediate.[12]

$$(CH_3)_2CH^+ + (CH_3)_2CHBr \rightarrow C_3H_6Br^+ + C_3H_8 \qquad (8)$$
$$(CH_3)_2CH^+ + (CH_3)_2CHBr \rightarrow ((CH_3)_2CH)_2Br^+ \qquad (9)$$

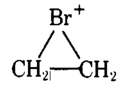
$$(CD_3)_2CH^+ + (CD_3)_2CHBr \rightarrow (CD_3)_2CBr^+ + (CD_3)_2CH_2 \qquad (10)$$
$$(CD_3)_2CH^+ + (CD_3)_2CHBr \not\rightarrow C_3HD_5Br^+ + (CD_3)_2CHD \qquad (11)$$

In *tert*-butyl bromide the only ion observed in the mass spectrum at 12.0 eV is the *tert*-butyl cation, $(CH_3)_3C^+$. The condensation reactions 12–15 occur with an overall rate constant $k = 0.4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. At higher pressures ($>10^{-4}$ Torr) ions of composition $C_9H_{19}{}^+$, $C_{10}H_{21}{}^+$, $C_{11}H_{23}{}^+$, $C_{12}H_{25}{}^+$, and $C_{13}H_{27}{}^+$ are also observed.[22]

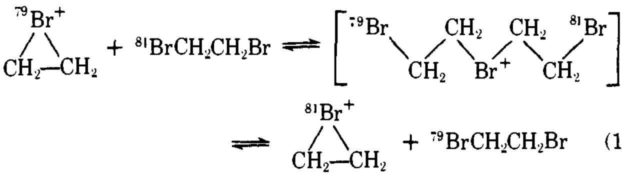
$$(CH_3)_3C^+ + (CH_3)_3CBr \xrightarrow{45\%} C_5H_{11}{}^+ + C_3H_7Br \qquad (12)$$
$$\xrightarrow{33\%} C_6H_{13}{}^+ + C_2H_5Br \qquad (13)$$
$$\xrightarrow{12\%} C_7H_{15}{}^+ + CH_3Br \qquad (14)$$
$$\xrightarrow{10\%} C_8H_{17}{}^+ + HBr \qquad (15)$$

Norbornyl cation and adamantyl cation are the predominant species in the 16.0-eV mass spectra of *exo*-2-norbornyl bromide and 1-adamantyl bromide, respectively. At higher pressures or longer delay times, reaction by minor fragment ions increases the abundance of these ions, which are not observed to undergo further reaction. The ion chemistry of 2-bromobutane, cyclopentyl bromide, acetyl bromide, and propionyl bromide is similar: R^+ is the predominant ion in the mass spectrum, the abundance of this species increases slightly with pressure or time due to reactions by minor fragments, and no fast bimolecular reactions of this ion are observed with the parent neutral.

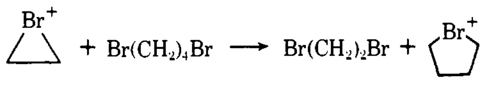
Dibromides. The principal ion (>80% at all electron energies) in the mass spectrum of $BrCH_2CH_2Br$ is $C_2H_4Br^+$ (*m/e* 107 and 109) corresponding to the cyclic bromonium ion.



The relative intensity of this ion is not observed to decrease with increasing pressure or trapping times, suggesting that it is unreactive. However, if the species at *m/e* 109 is ejected by use of the double resonance oscillator in a time short compared to the time between collisions, Figure 2, then the species at *m/e* 107 is observed to decay rapidly.[13] This indicates the rapid isotopic exchange reaction 16. The measured rate constant (average of three determinations) indicates, correcting for statistical factors, an overall rate constant for reaction of 5.2 $\times$ 10^{-10} cm^3 molecule^{-1} s^{-1}. The ion chemistry of other dibromides is similar, the rate constant for thermoneutral bromide exchange decreasing with increasing methyl substitution in the three-member rings. The thermoneutral isotopic exchange reaction was not observed in the five member ring bromonium ions.


(16)

Mixtures. In a binary mixture of organic bromides R_1Br and R_2Br, bromide transfer, reaction 4, provides a measure of the relative stability of the carbenium ions $R_1{}^+$ and $R_2{}^+$. Examination of the trapped ion spectra of these species in such mixtures establishes the preferred direction of reaction. For example, in a mixture of 1,2-dibromoethane and 1,4-dibromobutane, reaction 17 proceeds entirely to the right, Figure 3a.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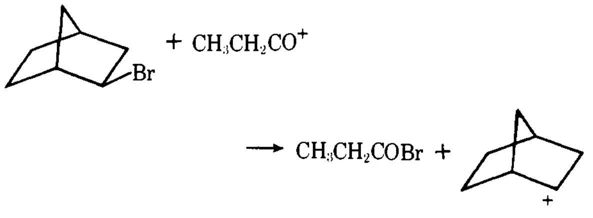

(18)

In reaction 18, *exo*-2-norbornyl bromide is observed to transfer Br^- to $CH_3CH_2CO^+$, Figure 3b. The inferred reactions are confirmed by double resonance experiments. For a series of carbenium ions R^+, similar experiments indicate the order for relative *free energies* of RBr heterolytic bond cleavage as shown in Chart I.[23]

Estimates of bromide affinities, $D(R^+\text{-}Br^-)$, from available thermochemical data considered in detail below are given in parentheses in kcal/mol. Also, in order to investigate the relative stabilities of several isomeric carbenium ions (see below), ion-molecule reactions in a mixture of $(CD_3)_2CHBr$ and $CH_3CHBrCH_2Br$ were examined; reaction 19 was not observed to occur.

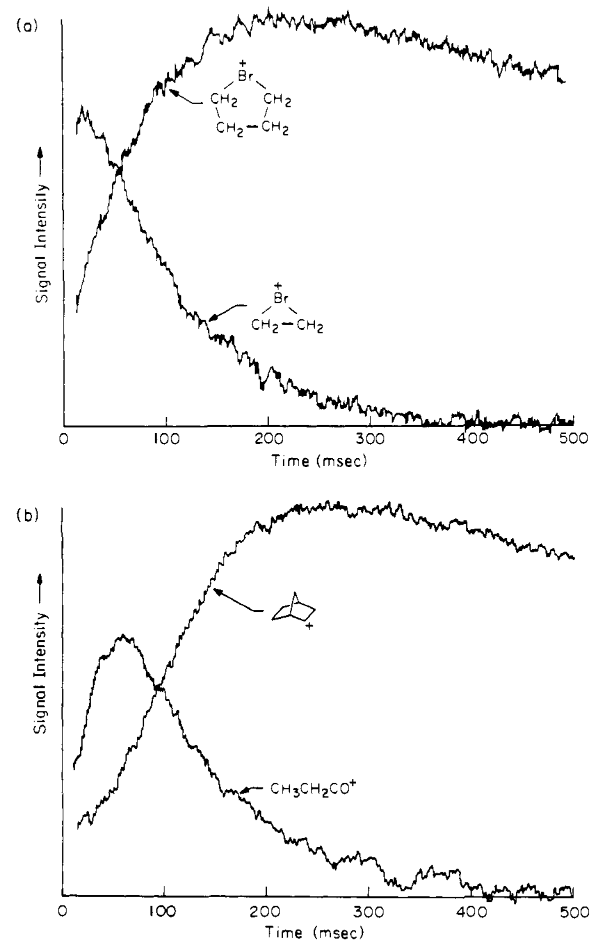
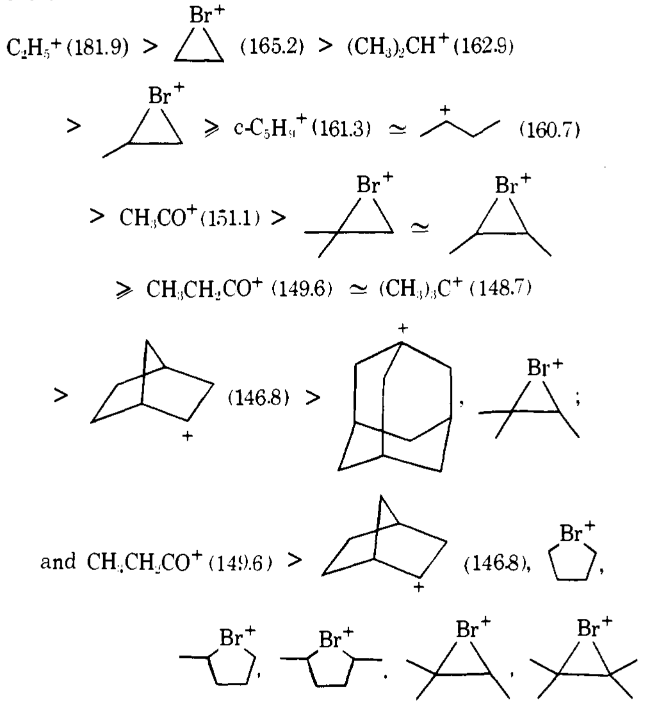


Figure 3. Variation of ion intensities with time in two mixtures of bromides. Relative carbonium ion stabilities in the gas phase with respect to Br^- are determined from the direction of Br^- transfer: (a) 6:1 mixture of 1,2-dibromoethane and 1,4-dibromobutane at a total pressure of 2×10^{-6} Torr: tetramethylenebromonium ion is more stable than ethylenebromonium ion (reaction 17); (b) 7:1 mixture of propionyl bromide and *exo*-2-norbornyl bromide at a total pressure of 3×10^{-6} Torr: norbornyl cation is more stable than propionyl cation (reaction 18). Buildup of the displayed species during the first 50 ms is due in part to reaction by fragment ions (not shown) following the initial 10 ms, 16 eV electron beam pulse.

Chart I



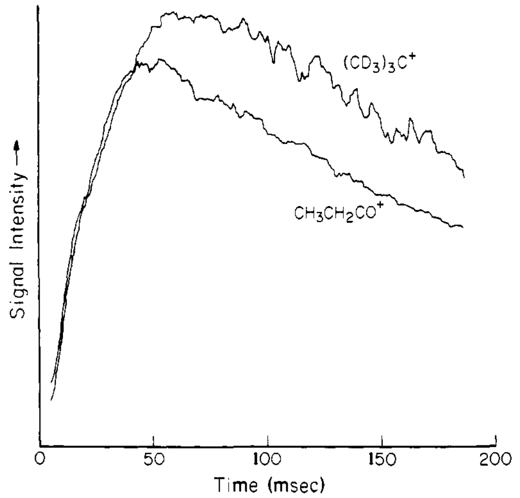
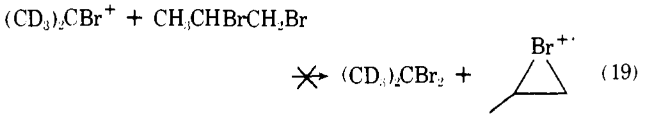


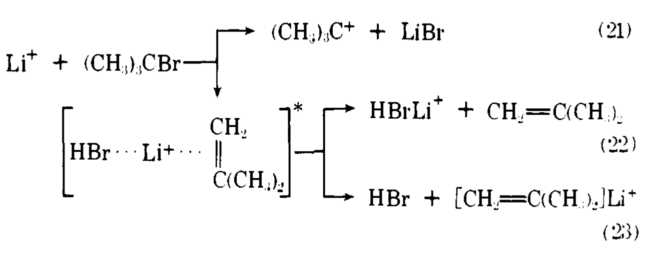
Figure 4. Variation of ion intensities with time for a mixture of $(CD_3)_3CBr$ (4.2×10^{-7} Torr) and CH_3CH_2COBr (5.4×10^{-7} Torr). A 10 ms, 18 eV electron beam pulse initiates ionization. The constant ratio of ion abundances after ~100 ms indicates establishment of equilibrium in Br^- transfer between $(CD_3)_3C^+$ and $CH_3CH_2CO^+$.



In one instance, reaction 20, an equilibrium was readily observed (Figure 4). Ion ejection experiments confirmed that the rates of forward and reverse Br^- transfer were rapid. The data shown in Figure 4 give $\Delta G = -0.23$ kcal/mol for reaction 20. Correcting for the isotope effect[24] ($(CH_3)_3C^+$ and $CH_3CH_2CO^+$ are both *m/e* 57, requiring the use of labeled reactants) gives $\Delta G \simeq \Delta H = -0.5 \pm 0.1$ kcal/mol for the analogue of reaction 20 involving $(CH_3)_3C^+$.

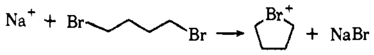
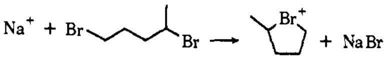
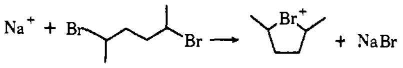
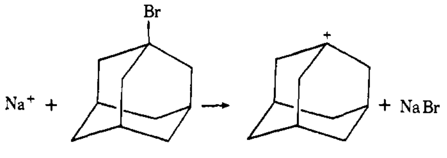
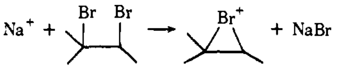
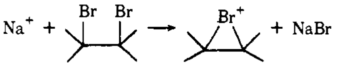
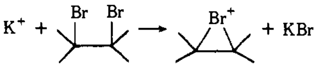
$$CH_3CH_2CO^+ + (CD_3)_3CBr \rightleftharpoons (CD_3)_3C^+ + CH_3CH_2COBr \quad (20)$$

Alkali Ion Reactions. The reactivity of the alkali cations Li^+, Na^+, and K^+ with various organic halides was investigated. Both bromide transfer and elimination reactions were observed. For example, with Li^+ and $(CH_3)_3CBr$, reactions 21–23 were observed. Further studies of the elimination processes 22 and 23 have been reported separately.[16,17] The bromide transfer reaction 21 is a special case of reaction 4 with $R_1^+ = M^+ = Li^+$ and may be used to infer limits on the relative stability of M^+ and R_2^+ with respect to the reference base X^-. The observed reactivity of alkali ions with various organic bromides is presented in Table I.



Photoionization Studies. Photoionization studies were performed in conjunction with the present work to better quantify heats of formation for several of the carbenium ions considered. Species examined include CH_3CHO, CH_3CH_2CHO, $(CH_3)_2CO$, 1,2-dibromoethane, and 1,4-dibromobutane. Measured ionization thresholds for molecular and selected fragment ions are summarized in Table II.

Table I. Reactions Investigated in Mixtures of Organic Bromides with Alkali Ions

Reaction	Observed reactivity[a]
$Li^+ + (CH_3)_2CHBr \xrightarrow{<1\%} (CH_3)_2CH^+ + LiBr$	Not observed
$\xrightarrow{100\%} [C_3H_6]Li^+ + HBr$	Fast
$Li^+ + CH_3COBr \longrightarrow CH_3CO^+ + LiBr$	Not observed
$Li^+ + (CH_3)_3CBr \xrightarrow{6\%} (CH_3)_3C^+ + LiBr$	Slow
$\xrightarrow{93\%} [C_4H_8]Li^+ + HBr$	Fast
$\xrightarrow{1\%} HBrLi^+ + C_4H_8$	Slow
$Li^+ + CH_3CH_2COBr \xrightarrow{68\%} CH_3CH_2CO^+ + LiBr$	Fast
$\xrightarrow{32\%} [CH_3CHCO]Li^+ + HBr$	Fast
	Not observed
	Not observed
	Not observed
	Not observed
	Not observed
	Fast
	Not observed

[a] Approximate rate constants have been inferred from observed ion intensities in ICR drift spectra and assigned to one of three ranges: fast, $k \gtrsim 10^{-10}$; slow, $10^{-10} \lesssim k \leqslant 10^{-12}$; not observed, $k < 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Table II. Summary of Photoionization Data for Selected Molecules

Molecule	Ion	Ionization threshold[a]	ΔH_f[b]
CH_3CHO			-39.7
	CH_3CHO^+	10.20	195.6
	CH_3CO^+	10.82	157.8
$(CH_3)_2CO$			-51.9
	$(CH_3)_2CO^+$	9.68	171.4
	CH_3CO^+	10.36	153.1
CH_3CH_2CHO			-45.5
	$CH_3CH_2CHO^+$	9.95	184.1
	$CH_3CH_2CO^+$	10.79	151.3
CH_2BrCH_2Br			-9.1
	$CH_2BrCH_2Br^+$	10.37	230.2
	$C_2H_4Br^+$	10.53	207.2
$Br(CH_2)_4Br$			-25.0[c]
	$Br(CH_2)_4Br^+$	10.15	209.2
	$(CH_2)_4Br^+$	10.15	$\leqslant$182.5[d]

[a] Threshold data in eV. [b] All data in kcal/mol. Neutral heats of formation from ref 37. [c] Estimated using group equivalents. [d] This is an upper limit to the true heat of formation (see text for discussion).

Ionization efficiency curves for $(CH_3)_2CO$ reproduce data reported in the literature.[25] The threshold for CH_3CO^+ formation of 10.36 eV gives $\Delta H_f(CH_3CO^+)$ = 153.1 kcal/mol. The threshold of 10.82 eV for CH_3CO^+ formation from CH_3CHO gives $\Delta H_f(CH_3CO^+)$ = 157.8 kcal/mol, which is substantially higher than the value obtained from acetone.[26] If $\Delta H_f(CH_3CO^+)$ from acetone were correct, then $D(CH_3CO^+\text{-}Br^-)$ = 146.4 kcal/mol is less than $D[(CH_3)_3C^+\text{-}Br^-]$, in disagreement with the experimental ordering of heterolytic bond dissociation energies. Using $\Delta H_f(CH_3CO^+)$ derived from acetaldehyde gives $D(CH_3CO^+\text{-}Br^-)$ = 151.1 kcal/mol, which agrees with the experimental ordering. In addition, a recent study of the proton affinity of ketene gives $\Delta H_f(CH_3CO^+) = 159.2 \pm 2$ kcal/mol, in close agreement with the value derived from acetaldehyde.[27]

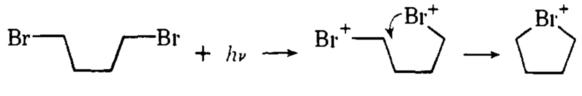
The above discrepancy could result from a thermal shift in the case of acetone (where ionization and dissociation of molecules with excess internal energy yields a threshold lower than the true thermodynamic threshold) or from a significant kinetic shift in the case of acetaldehyde (giving a threshold higher than the true thermodynamic value). The rather low abundance of CH_3CO^+ from both molecules in the threshold region further suggests that fragmentation of the molecular ion results from autoionizing states which yield a molecular ion with sufficient internal energy for fragmentation to occur.

A similar discrepancy occurs in the determination of $\Delta H_f(CH_3CH_2CO^+)$, with the value being 7.4 kcal/mol higher from CH_3CH_2CHO than from $CH_3CH_2COCH_3$. Again the value derived from the aldehyde gives best agreement, with the derived $D(CH_3CH_2CO^+\text{-}Br^-)$ = 149.6 kcal/mol being very close to the value of 148.7 kcal/mol for $D[(CH_3)_3C^+\text{-}Br^-]$. As noted above, an equilibrium is observed for this system, giving a measured difference of 0.5 kcal/mol, in excellent agreement with the calculated difference of 0.9 kcal/mol.

In the present work the heats of formation adopted for acylium ions are those derived from aldehydes and not from ketones. The discrepancies noted deserve further attention to better understand their origin; there is no reason to believe that they result from uncertainties in neutral heats of formation.

The threshold for generating the ethylenebromonium ion from 1,2-dibromoethylene occurs 0.16 eV above the ionization threshold for the molecular ion (Table II). The heterolytic bond dissociation energy $D(R^+\text{-}Br^-)$ can be calculated by subtracting EA(Br) from the measured threshold, giving a value of 165.2 kcal/mol. This is in good agreement with the relative values discerned from halide transfer experiments. The threshold for the tetramethylenebromonium ion coincides with the adiabatic ionization potential of 10.15 eV. This provides only the limit $D(R^+\text{-}Br^-) \leqslant 165.4$ kcal/mol. The bromide transfer experiments indicate a value substantially smaller. Ionization of 1,4-dibromobutane involves formation of a molecular ion in which there is initially no substantial interaction between the two bromine centers.[28] Subsequent to ionization an exothermic reaction takes place between the two bromine centers (Scheme I) to form cyclic halonium ions. The latter process is analogous to the exothermic bimolecular reaction 3 of the monobromides which leads to formation of an acyclic bromonium ion. The energy release (estimated to be ~20 kcal/mol) in the displacement reaction is not revealed in the photoionization fragmentation threshold. Formation of the more highly strained bromonium ion from 1,2-dibromoethane requires excess internal excitation in the molecular ion. Interestingly, the molecular ion of 1,4-dibromobutane is readily detected, and indicates that not all of the initially formed molecular ions decompose as indicated in Scheme I.

Scheme I

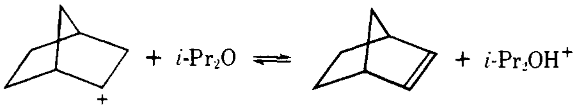


Proton Affinity of Norbornene. The bromide affinity of norbornyl cation may be calculated from the proton affinity of norbornene. Proton affinity (PA) is defined for a base B as the heterolytic bond dissociation energy for removing a proton from the conjugate acid BH^+, eq 24.[29-33] Kaplan, Cross, and Prinstein investigated the proton affinity of norbornene and reported a value of 207 kcal/mol.[34] Accurate relative values of proton affinity may be determined by measuring equilibrium constants for proton transfer, reaction 25.[29-33]

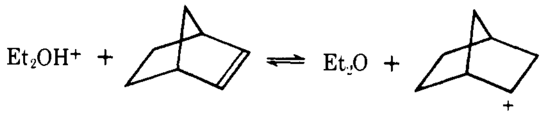
$$BH^+ \rightarrow B + H^+ \qquad \Delta H = D(B\text{-}H^+) \equiv PA(B) \quad (24)$$

$$B_1H^+ + B_2 \rightleftharpoons B_1 + B_2H^+ \qquad \Delta H = PA(B_1) - PA(B_2) \quad (25)$$

Proton transfer reactions in mixtures of norbornene with various bases were examined. Reaction 26 was observed to proceed entirely to the right ($K > 300$), establishing an upper limit of 203.8 kcal/mol for PA(norbornene). For reaction 27,



(26)



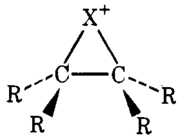
(27)

an equilibrium constant of $K = 2.3 \pm 0.3$ was measured, average of three determinations, from which PA(norbornene) = 198.8 kcal/mol is calculated. All of the quoted values of proton affinity are with respect to $PA(NH_3) = 202.3 \pm 2.0$ kcal/mol which has been established by experiments in which $PA(NH_3)$ is obtained relative to several molecules for which absolute values of proton affinity are known from appearance potential measurements or ionization potentials of the corresponding radicals.[33]

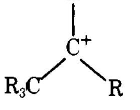
The measured proton affinity gives $\Delta H_f = 189.1$ kcal/mol for the norbornyl cation. From studies of hydride transfer equilibria, Solomon and Field have determined $\Delta H_f = 187.3$ kcal/mol for the norbornyl cation.[15] The agreement is excellent in view of the uncertainties in reference data for both experiments, namely, the proton affinity of ammonia and the heat of formation of the *tert*-butyl cation.

Discussion

Relative Stabilities of Structural Isomers. The relative stabilities of bridged and open haloalkyl cation isomers, structures I and II, depend on the sizes and positions of the alkyl substituents, R = H, Me, Et, etc., and the particular halogen considered, X = F, Cl, Br.[6,35] Extrapolation of theoretical results for fluoro- and chloroethyl cations suggests that for the bromoethyl cation, the isomer of structure III is more stable than IV.[35] While cyclic bromo- and iodoalkyl cations, structure I, X = Br, I, have been well characterized in solution by ^1H and ^{13}C NMR, the existence of the open forms as stable species is questionable.[6]

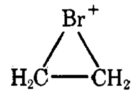


I

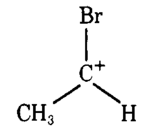


II

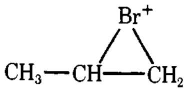
Two isomeric ions of the formula $C_3H_6Br^+$ are encountered in the present work, structures V and VI. In $(CH_3)_2CHBr$ the observed reaction of $(CH_3)_2CH^+$, reaction 8, implies a heat of formation for the product $C_3H_6Br^+$ of $\Delta H_f \leqslant 193.0 \pm 2$ kcal/mol.[36,37] Since hydride abstraction occurs exclusively from the 2 position, reaction 10, this ion must have structure VI. The observed direction of reaction 8 shows that the carbenium ion center is stabilized by Br substitution, consistent with previous studies which indicate that halogen substitution on carbenium ions is stabilizing when stabilities are defined with respect to the reference base H^-.[12,13,38] The $C_3H_6Br^+$ ion formed from 1,2-dibromopropane is expected to have structure V. From the bromide affinity of this ion (see below) a value of 194.5 ± 2 kcal/mol may be calculated for its heat of formation,[37,39,40] which suggests that this isomer is somewhat less stable than the isomer with structure VI for which $\Delta H_f \leqslant 193.0 \pm 2$ kcal/mol. A direct comparison of the stabilities of these ions with respect to the reference base Br^-, reaction 18, is also consistent with this result: the ion with structure VI does not react with $CH_3CHBrCH_2Br$ to give V. Observation of the reversible bromide exchange reaction for 1,2-dibromopropane, analogous to reaction 16 in 1,2-dibromoethane, suggests, however, that the cyclic isomer V retains its structural integrity and does not rearrange to the more stable isomer VI.



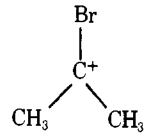
III



IV



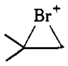
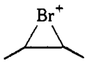
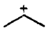
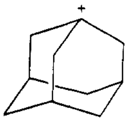
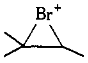
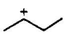
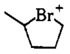
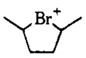
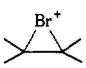
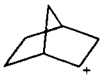
V



VI

Bromide Affinities. Reference values of bromide affinity to calibrate the scale of relative bromide affinities established by

Table III. Heterolytic $R^+{-}X^-$ Bond Dissociation Energies

R^+	$D(R^+{-}Br^-)$[a]	R^+	$D(R^+{-}Br^-)$[a]
CH_3^+	217.7 ± 2[b,c]		146.8 ± 2
$C_2H_5^+$	181.9 ± 2[b,c]		146.4 ± 2
	165.2 ± 2	$CH_3CH_2CO^+$	149.6 ± 2[e]
	162.9 ± 2[b,c]		137.9 ± 10
	161.3 ± 2[b,d]		135.0 ± 10
	160.7 ± 2[b,c]		133.6 ± 10
	159.6 ± 2		133.6 ± 10
CH_3CO^+	151.1 ± 2[b,e]		133.6 ± 10
Li^+	148.7 ± 3[f]	Na^+	127.9 ± 1[f]
$(CH_3)_3C^+$	148.7 ± 2[b,c]		117.8 ± 7
	146.8 ± 2[g]	K^+	113.7 ± 1[f]

[a] All data in kcal/mol. [b] References 37, 39, and 40. [c] Reference 36. [d] Reference 41. [e] See text for discussion. [f] References 39 and 40. [g] Present work and ref 34 and 42; see text.

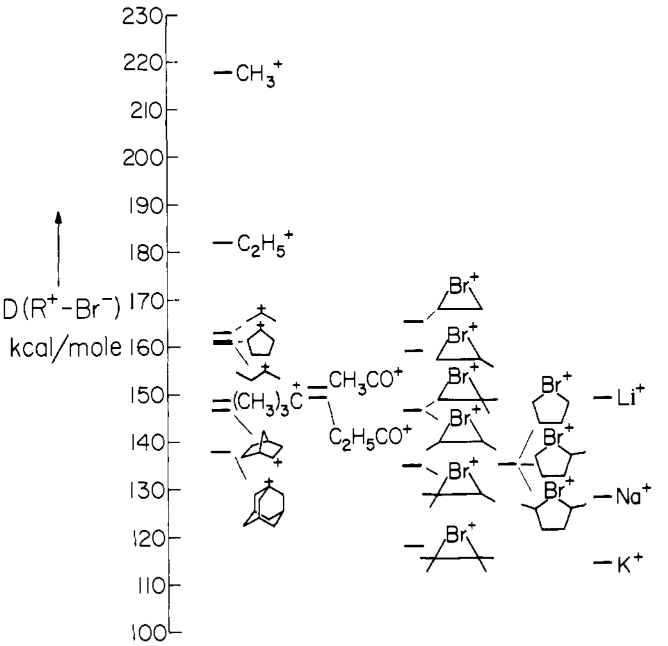
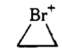
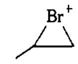
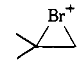
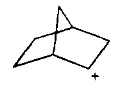
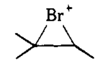
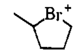
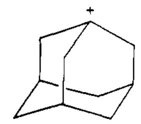
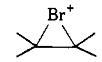


Figure 5. Gas phase bromide affinities of alkyl carbenium ions, acyl cations, cyclic bromonium ions, and alkali cations.

Table IV. Relative Heats of Ionization in Magic Acid Solution[a]

Ion	$\Delta\bar{H}_{S,CCl_4}$	$\Delta H_i(l)$[b]	ΔH_{vap}[c]
Bromide Precursors[d] $RBr \rightarrow R^+ + Br^-$			
	0.2	+1.0	9.9
	0.1	−3.3 ± 0.5	9.8
	0.0	−8.4 ± 0.9	10.6
$(CH_3)_3C^+$	0.1	−14.5 ± 2.0	7.4
	2.2	−13	11.0
	−0.3	−13.4 ± 0.9	11.5
	0.3	−13.8 ± 1.9	13.0
	3.8	−14.3 ± 0.2	18.3[d]
	2.4	−22.9 ± 4.0	15.8
Chloride Precursors[e] $RCl \rightarrow R^+ + Cl^-$			
$(CH_3)_3C^+$	0.2	−6.7 ± 0.2	6.9
CH_3CO^+	1.0	−21.2 ± 0.2	7.2
$C_2H_5CO^+$	0.8	−19.4 ± 0.3	8.3

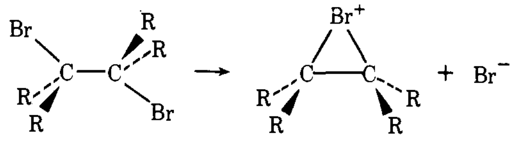
[a] All data in kcal/mol. Magic acid refers to HSO_3F containing ca. 11% SbF_5. [b] Data from ref 8, 49, and 50; the symbol ΔH_{obsd} is used in ref 8 for $\Delta H_i(l)$ defined in the present work. [c] Data from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970; or estimated from boiling point data. [d] 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. Am. Chem. Soc.*, 92, 2377 (1970), as described in A. Bondi, *J. Chem. Eng. Data*, 8, 371 (1963). [e] Data from ref 7.

studies of reaction 4 are available from several sources. Heats of formation for a number of alkyl carbenium ions are available from the work of Lossing, who has measured ionization potentials for the corresponding radicals.[36,41] Heats of formation for the acyl cations CH_3CO^+ and $CH_3CH_2CO^+$ are derived in the present study as discussed above. All of these values may be combined with values for the heats of formation for the corresponding neutral bromides[37] and $\Delta H_f(Br^-) = -52.3$ kcal/mol[39,40] to give bromide affinities, Table III. Bromide affinity values for the alkali ions Li^+, Na^+, and K^+ are also available in the literature, Table III.[40] The experimental results from studies of reaction 4 are all consistent with these values.

From the measured proton affinity of norbornene, PA(norbornene) = 198.8 ± 2 kcal/mol, the reported heat of hydrogenation of norbornene to norbornane of 33.13 ± 0.21 kcal/mol,[42] and the difference in heats of formation of norbornane and *exo*-2-norbornyl bromide of $\Delta\Delta H_f = -2.4 \pm 1$ kcal/mol estimated from group heats,[37] a bromide affinity for norbornyl cation of 146.8 ± 2.3 kcal/mol is calculated.

The relative order of free energies for process 4 established by the observed bromide transfer reactions may be combined with the results from the alkali ion studies and the calculated values for $D(R^+-Br^-)$ for the reference compounds to obtain bromide affinities for all of the compounds studied, Table III, Figure 4.[43] Enthalpies of bromide transfer are 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,[29-33] ΔS will be small for processes such as reaction 18 but cannot be ignored in processes such as reaction 17 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 alkali ions, alkyl carbenium ions, and acyl cations.[44]

The effect of methyl substitution in the three member ring bromonium ion series is interesting since each successive substitution appears to have a larger stabilizing effect, with an average increase of about 12 kcal/mol per methyl group. The stabilizing effect of methyl substitution in this series is nearly as large as is found in methyl substitution of carbenium ions where from ethyl to isopropyl carbenium ions $D(R^+-Br^-)$ decreases by 19.0 kcal/mol and from isopropyl to *tert*-butyl 14.2 kcal/mol. Comparable results are also found in the effects of methyl substitution on proton affinity in the phosphine and arsine series (13.4 and 12.3 kcal/mol per methyl, respectively).[30,45] However, in these series the effect is smaller for larger members of the series. The unusual methyl substituent effect observed for the bromium ion series may in part be due to the increased effect of steric factors which destabilize the neutral relative to the ion, process 28, as H is replaced by

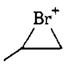
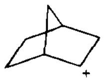
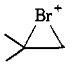
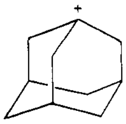
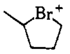
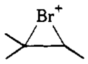
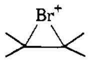


(28)

methyl. The five member ring tetramethylenebromonium ion is about 12 kcal/mol more stable than the isomeric dimethylethylenebromonium ion, reflecting reduced ring strain in the larger ring.[46]

Also of particular interest is the result for adamantyl cation, which is found to be more stable than *tert*-butyl cation. This indicates that the strain energy due to the nonplanarity of the carbenium ion center in the 1-adamantyl carbenium ion relative to the *tert*-butyl carbenium ion is smaller than the stabilization afforded by the interaction of the charge with the

Table V. Estimated Relative Enthalpies of Solution of R^+ in HSO_3F[a]

R^+	$\Delta H_S(R^+) + \Delta H_S(Br^-)$[b]	$\delta_R \Delta H_S(R^+)$[c]
CH_3CO^+	−186.8 ± 3	−16
	−173.9 ± 2	−3
$CH_3CH_2CO^+$	−184.8 ± 6	−14
	−172.6 ± 1	−2
$(CH_3)_3C^+$	−170.5 ± 2	0
	−168.6 ± 3[d]	2[d]
	−165.8 ± 2	5
	−166.7 ± 10	4
	−160.1 ± 10	10
	−160.2 ± 10	10
	−154.1 ± 8	16

[a] All data in kcal/mol. [b] Calculated using the thermochemical cycle 29 and eq 30 and 31 with the data in Tables III and IV. [c] Heats of solvation of R^+ relative to that of $(CH_3)_3C^+$. [d] See footnote 51.

added hydrocarbon framework.[47] It would be of interest to refine the measurement of the heat of formation for adamantyl cation to better quantify this difference.

Solvation Energetics. The thermochemical cycle 29 where g and l designate the gas and liquid phases and subscripts i and s designate ionization and solution processes, respectively, may be employed to obtain heats of solvation of R^+, $\Delta H_s(R^+)$, if the other quantities are known.[48] Values for $\Delta H_i(g)$ are available from the present work. Heats of ionization in solution $\Delta H_i(l)$ are available for a number of the ions examined in this study from calorimetrically determined heats of solution of RX in magic acid solution (HSO_3F containing ca. 11% SbF_5), Table IV,[7,8,49-51] where the quantity actually measured is the heat of transfer from dilute solution in CCl_4 at 25 °C to the acid at −60 °C. Heats of solution, $\Delta H_s(RBr)$, are obtained by correcting heats of solution in carbon tetrachloride, $\Delta \overline{H}_s$, CCl_4, for the heat of vaporization (or sublimation) of RBr.

$$\begin{tikzcd}
RBr(g) \arrow[r, "\Delta H_i(g)"] \arrow[d, "\Delta H_s(RBr)"'] & R^+(g) \arrow[d, "\Delta H_s(R^+)"'] & + & Br^-(g) \arrow[d, "\Delta H_s(Br^-)"'] \\
RBr(l) \arrow[r, "\Delta H_i(l)"] & R^+(l) & + & Br^-(l)
\end{tikzcd} \tag{29}$$

$$\Delta H_S(RBr) = \Delta \overline{H}_s, CCl_4 - \Delta H_{vap} \tag{30}$$

$\Delta H_i(l)$ from chloride precursors are converted to values for ionization of RBr by reference to the value for $R^+ = (CH_3)_3C^+$. Estimated relative enthalpies of solution of R^+ in magic acid, Table V, may be calculated using the data from Tables III and IV and eq 31, which is derived from the thermochemical cycle 29.

$$\Delta H_s(R^+) + \Delta H_s(Br^-) = -\Delta H_i(g) + \Delta H_i(l) + \Delta H_s(RBr) \tag{31}$$

It is apparent from these data that solvation enthalpies are related to ion size; smaller ions are better solvated. A direct comparison of $D(R^+\text{-}Br^-)$ in the gas phase and solution is also revealing. The relative bromide affinities of cyclic bromonium ions are the same in the gas phase and solution. Stability increases with increasing ring size and, in the three-membered rings, methyl substitution. However, solvent has an appreciable effect in attenuating the observed range.

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Reaction of 1,1-Diphenyl-2-vinylcyclopropane with Tetracyanoethylene, Diene, Diborane, and Dibromocarbene. Formation of Unusual Adducts after Rearrangements Supporting a Two-Step Process[1,2]

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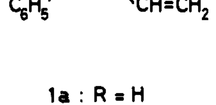
Abstract: 1,1-Diphenyl-2-vinylcyclopropane (**1a**) reacts with tetracyanoethylene yielding *N*-diphenylmethylene-2,3,3-tricyano-5-vinylcyclopent-1-enylamine (**2a**) as a major adduct. The related ethylene **1c** produces fluorenylideneamine **2c** and the chain adduct **4a**. The expected cycloadducts did not form in both cases. In contrast, the Diels–Alder reaction of **1a** with tetrachlorocyclopentadienone ethylene acetal gives the normal cycloadduct **6c**. Hydroboration-oxidation and dibromocarbene addition also yield expected products, 2-(2,2-diphenylcyclopropyl)ethanol (**7**) and a pair of bicyclopropyls (**8a** and **8b**), respectively. It can thus be concluded that the concerted processes preserve the 2,2-diphenylcyclopropyl group. The reactions of vinylcyclopropanes with TCNE are, therefore, not a concerted but a stepwise reaction, in which extensive rearrangements take place. A probable path to **2** and **4** is proposed.

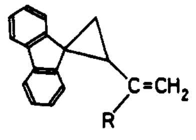
It has been recently demonstrated that the utilization of vinylcyclopropane derivatives as a substrate in the investigation of radical cycloadditions to a carbon–carbon double bond permits us to discuss the intermediacy of a diradical species in such reactions.[3] It is hoped presently that similar demonstrations can also be made in cycloaddition reactions involving a dipolar intermediate.[4,5] Thus the reactions of 1,1-diphenyl-2-vinylcyclopropane (**1a**) and the related ethylenes (**1b–d**) with tetracyanoethylene (TCNE) were examined and the results are compared with those of Diels–Alder, hydroboration-oxidation, and singlet carbene addition reactions. Both stepwise[5a,l] and concerted processes[6] have been discussed for the related TCNE cycloadditions.

Results

Reaction of 1a–d with Tetracyanoethylene. The reaction of **1a** with TCNE proceeded slowly at room temperature yielding an adduct of unexpected structure.[7] Thus, after a 1:1 mixture



1a: R = H
1b: R = CH_3



1c: R = H
1d: R = CH_3