of saturated sodium carbonate, giving a 44:56 mixture of **5**(4-Br) : *p*-bromoaniline. Two repetitions of the procedure gave after distillation a 60% overall yield of **5**(4-Br) as a 9 : 1 mixture with starting material.

***N-tert*-Butyl-*N*-nitroso-4-bromoaniline (6(4-Br)).** A solution of 9.1 g of sodium nitrate in 32 ml of water was added to 10 g of 90% *tert*-butylated aniline (**5**(4-Br), 0.039 mol) suspended in 18 ml of concentrated hydrochloric acid and 50 g of ice. The mixture was stirred for 2 hr in an ice bath, filtered, and crystallized from ethanol, giving **6**(4-Br); ir, no NH; satisfactory analyses were obtained for $C_{10}H_{13}BrNO$.

***N-tert*-Butyl-*N*-4-bromophenylhydrazine (7(4-Br)).** **6**(4-Br) (4 g, 0.155 mol) in 7 ml of acetic acid was added to 21 g of activated[23] zinc dust in 7 ml of water, keeping the mixture under 10°. After stirring 2 hr, the mixture was filtered, the cake washed with three 10-ml portions of 5% hydrochloric acid, and the filtrate basicified with 100 ml of 20% sodium hydroxide and extracted with five 10-ml portions of ether. The residue after solvent removal consisted of 3.2 g of a 60 : 40 mixture of hydrazine and amine.

1,4-Di-*tert*-butyl-1,4-bis(4-bromophenyl)-2-tetrazene (8(4-Br)). To 3.2 g of the above hydrazine–amine mixture (*ca.* 7.5 mmol) in 60 ml of absolute ethanol was added 0.95 g (8.8 mmol) of thrice-sublimed quinone in ethanol at −10°. The mixture was stirred for 2 hr at −10°, the ethanol was vacuum distilled out of the cold reaction mixture, and the residue was washed with ethanol, cooled to −78° until white, and crystallized from ethanol.

***N-tert*-Butyl-*p*-cyanoaniline (5(4-CN)).** A mixture of 25 g (0.11 mol) of **5**(4-Br) in 150 ml of dimethylformamide and 16 g (0.18 mol) of cuprous bromide was refluxed 36 hr, cooled, and poured into 200 g of sodium cyanide in 600 ml of water. The organic layer was separated and the aqueous solution extracted with 250 ml of benzene. The combined organic layers were washed with 200 ml of sodium cyanide and dried over sodium sulfate, the solvent was removed, and the residue was crystallized from water.

Esr spectra were recorded on Varian E-3 or E-15 equipment, the splittings and *g*-factors calibrated with Fremy's salt. Samples in 3-mm quartz tubes were irradiated with a 2.5-kW Hanovia mercury–xenon lamp filtered by 15 cm of a cobalt–nickel salt mixture, or with a Bausch and Lomb high intensity monochromator and an Osram SP-200 lamp.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, the Sloan Foundation, and the Wisconsin Alumni Research Foundation for generous support of this research, and the National Science Foundation for Departmental Major Instrument funds. We also thank Mr. James Kinsey for synthesis of **8**(4-Cl).

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Thermodynamic Stabilities of Some Cyclic Halonium Ions in Magic Acid[1]

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Abstract: The heats of formation of a series of methyl-substituted ethylene- and tetramethylenebromonium ions and a chloronium ion from the appropriate dihaloalkane precursors were measured calorimetrically in 11.5 mol % SbF_5–FSO_3H solution at −60°. The tetramethylenebromonium ions are about as stable as the *tert*-butyl cation and are *ca.* 10 kcal/mol more stable than a correspondingly substituted ethylenebromonium ion. The tetramethylenechloronium ion is *ca.* 7.5 kcal/mol less stable than its bromo analog. The interaction of a methyl group with a three-membered ring seems to be unusually favorable.

One of the most thoroughly studied families of organic intermediates is the cyclic halonium ions. However, there has been no information available on their thermodynamic stability. Accordingly, we have measured calorimetrically the heats of formation of a series of halonium ions from dihalide precursors in 11.5 mol % SbF_5–FSO_3H solution at −60°.

Several lines of evidence point to the existence of halonium ions as intermediates in a variety of reactions. The evidence for bromonium ions as intermediates in the addition of bromine to olefins is substantial and generally accepted.[2] Winstein developed a convincing case for the intermediacy of cyclic three-membered bromonium and iodonium ions through a detailed analysis of the solvolysis rates of *trans*-2-halocyclohexyl brosylates.[3] No evidence for chloronium ions was found.[4] Peterson has demonstrated the intermediacy of five-membered ring halonium ions in the addition of trifluoroacetic acid to 5-haloolefins.[5–10] In this work, good evidence for the chloronium ion as well as the bromonium and iodonium ions was obtained. Later work by both Peterson and Trahanovsky gave evidence for the same intermediates in solvolysis reactions.[11–13] In addition to their observation as unstable intermediates, stable halonium ion salts have been isolated.

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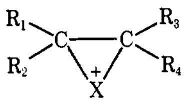
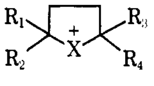
The diphenyliodonium ion has been known for nearly 60 years[14] while the diphenylchloronium and bromonium ions were first prepared nearly 20 years ago.[15] Very recently the preparation of stable alkyl-substituted halonium ions has been reported.[16–19]

Of more direct interest to our studies is the observation of stable cyclic halonium ions in strongly acidic media at low temperatures. Olah first reported the observation of the nmr spectra of the tetramethylethylene halonium ions **1a**, **b**, and **c** in SbF_5–SO_2 solution at −60°.[20] There have been some questions concerning the structure of ion **1b**,[21] but recent ^{13}C nmr evidence shows that the indicated structure is the correct one.[22] Using dihaloalkane precursors, Olah has generated ions **2**–**6**. When one of the R groups is phenyl rather than alkyl, a cyclic bromonium ion does not form, although there is nmr evidence for bromine participation.[24] Ions **1a** and **5a** have been prepared by protonation of cyclopropyl halides in FSO_3H–SbF_5–SO_2 solution.[25] In addition, **1a**–**c**[20] and **3b**[23] have been reported in FSO_3H–SbF_5–SO_2 mixtures.



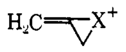
1a,[20,21] $R_1 = R_2 = R_3 = R_4 =$ Me; X = Cl
b, $R_1 = R_2 = R_3 = R_4 =$ Me; X = Br
c, $R_1 = R_2 = R_3 = R_4 =$ Me; X = I
2a,[23] $R_1 = R_2 = R_3 =$ Me; $R_4 =$ H; X = Cl
b, $R_1 = R_2 = R_3 =$ Me; $R_4 =$ H; X = Br
c, $R_1 = R_2 = R_3 =$ Me; $R_4 =$ H; X = I
3a,[23] $R_1 = R_2 =$ Me; $R_3 = R_4 =$ H; X = Br
b, $R_1 = R_2 =$ Me; $R_3 = R_4 =$ H; X = I
4a,[24] $R_1 = R_3 =$ Me; $R_2 = R_4 =$ H; X = Br cis
b, $R_1 = R_3 =$ Me; $R_2 = R_4 =$ H; X = I trans
5a,[24] $R_1 =$ Me; $R_2 = R_3 = R_4 =$ H; X = Br
b, $R_1 =$ Me; $R_2 = R_3 = R_4 =$ H; X = I
6a,[21,24] $R_1 = R_2 = R_3 = R_4 =$ H; X = Br
b, $R_1 = R_2 = R_3 = R_4 =$ H; X = I

In addition to the ethylenehalonium ions, the tetramethylenehalonium ions **7**–**10** have been studied.

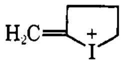


7a,[26] $R_1 = R_2 = R_3 = R_4 =$ H; X = Cl
b, $R_1 = R_2 = R_3 = R_4 =$ H; X = Br
c, $R_1 = R_2 = R_3 = R_4 =$ H; X = I
8a,[26] $R_1 =$ Me; $R_2 = R_3 = R_4 =$ H; X = Cl
b, $R_1 =$ Me; $R_2 = R_3 = R_4 =$ H; X = Br
c, $R_1 =$ Me; $R_2 = R_3 = R_4 =$ H; X = I
9a,[27] $R_1 = R_2 =$ Me; $R_3 = R_4 =$ H; X = Cl
b, $R_1 = R_2 =$ Me; $R_3 = R_4 =$ H; X = Br
c, $R_1 = R_2 =$ Me; $R_3 = R_4 =$ H; X = I
10a,[26] $R_1 = R_3 =$ Me; $R_2 = R_4 =$ H; X = Cl
b, $R_1 = R_3 =$ Me; $R_2 = R_4 =$ H; X = Br
c, $R_1 = R_3 =$ Me; $R_2 = R_4 =$ H; X = I

Olah and Peterson have observed formation of ions **7** and **8** from 1,4-dihalobutanes and 1,4-dihalopentanes, respectively, in SbF_5–SO_2 solution at −60°.[26] Ions **9a**–**c** were produced from a variety of precursors in both SbF_5–SO_2 and FSO_3H–SbF_5–SO_2.[27] Also, **10a**–**c** were formed by protonating 5-halo-1-hexenes in FSO_3H–SbF_5–SO_2.[26] In addition, the alkylation reactions of a number of cyclic tetramethylenehalonium ions have been studied.[28] Quite recently, noncyclic dialkylhalonium ions have been observed.[16–19] The interesting ions **12a**–**c** and **13** have also been prepared.[29]



12a, X = Cl
b, X = Br
c, X = I



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There is abundant evidence for the intermediacy of halonium ions in a variety of reactions and for their existence as stable species in superacid media. In order to better understand the bonding and chemistry of these intermediates, we undertook calorimetric measurements of their heats of formation from dihalides in a superacid system at −60°.

Results and Discussion

It is first necessary to verify that the desired halonium ions are formed under the conditions existing in the calorimeter, that is, in a solution of 11.5 mol % SbF_5 in FSO_3H at −60°. All of the ions prepared in the course of this work had been observed previously in SbF_5–SO_2 solutions or in FSO_3H–SbF_5–SO_2 solution at −60°. We prepared ions **2b**, **3a**, **8a**, and **8b** in 11.5 mol % SbF_5–FSO_3H and observed the same nmr spectra reported by Olah. Thus, at least one ion of each type discussed here has been observed in the solvent system used for calorimetry. The nmr spectra of ions **8a** and **8b** showed small broad peaks at δ 3.30 and 3.20, respectively, in addition to the peaks assigned to the halonium ions. These small peaks probably resulted from decomposition of the ion. We were not able to observe a clean nmr spectrum of the methylethylenebromonium ion **5a**. The light yellow solution formed upon introduction of the sample into the acid darkened rapidly as the solution was transferred to the nmr tube. This ion seemed particularly sensitive to warming.

We feel that it is possible to produce ions in the calorimeter which are observed only with difficulty in the same solvent using nmr. In the calorimeter, very low (*ca.* 10^{-3} *M*) concentrations are used. A small amount of sample is introduced into a very rapidly stirred solution largely doing away with local heating effects. All of these factors will favor the formation of ions in the calorimeter over the formation of the same ion at the high concentrations necessary for nmr observation. Of course, no information about the structure of an ion can be gained from a calorimeter.

The decomposition or polymerization of an ion of low thermodynamic stability in the calorimeter is readily apparent. Both our nmr studies and Olah's indicate that 1,2-dichloropropane polymerizes in magic acid.[30] We observed a heat of reaction of −29 kcal/mol for this compound. This is 15 kcal/mol more exothermic than

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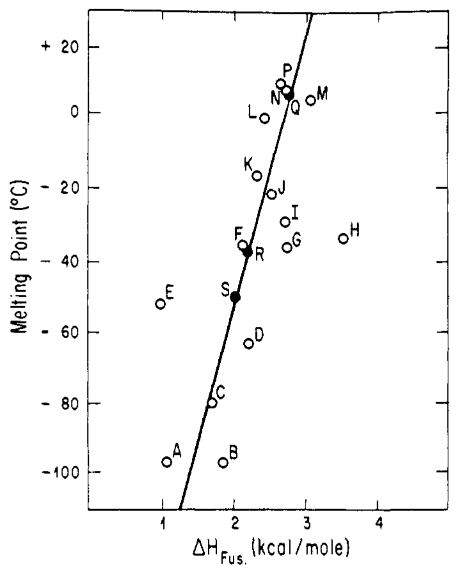
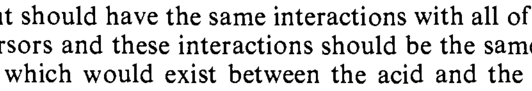


Figure 1. Heats of fusion *vs.* melting point for polyhalohydrocarbons: A, CH_2Cl_2; B, $CHCl_2CH_3$; C, $CHCl{=}CHCl$; D, $CHCl_3$; E, CH_2Br_2; F, CH_2ClCH_2Cl; G, $CHCl_2CH_2Cl$; H, $CH_2BrCH_2CH_2Br$; I, CCl_3CHCl_2; J, $CCl_2{=}CCl_2$; K, CH_2ClCH_2Br; L, $CHBr_2CHBr_2$; M, CH_2I_2; N, $CHBr_3$; P, CH_2BrCH_2Br; Q, $(CH_3)_2CBrCHBrCH_3$; R, $CH_3CHBrCH_2CH_2CHBrCH_3$; S, $(CH_3)_2CFCHBrCH_3$.

the formation of the chloronium ion reported and obviously too exothermic to be associated with halonium ion formation. We could not obtain reproducible calorimetric data for 1,4-dibromobutane, 2,3-dibromobutane, and 1,2-dibromoethane. The measurements were badly scattered and included some highly exothermic values. We conclude that under the conditions used in this study, the formation of these halonium ions is not clean and is probably complicated by polymerization which varies with sample introduction.

The quantity of interest to us is the heat of formation of a halonium ion from a covalent precursor in magic acid at −60° as illustrated by eq 1.[31] It is not possible



(1)

to use a dilute solution of the dihalide in the acid as the standard state, since the dihalides ionize rapidly upon introduction into the acid. What is necessary is a standard state in which all of the dihalides are in solution[32] and are not ionized. Furthermore, the reference solvent should have the same interactions with all of the precursors and these interactions should be the same as those which would exist between the acid and the unionized precursor.[33,34] This is quite impossible and some compromise must be reached. As before,[35,36] we have adopted carbon tetrachloride at 25° as the standard state. Some of the solvent–solute interactions will be similar in carbon tetrachloride and the acid,[34] but the transfer of all of the precursors from carbon tetrachloride to the acid is not expected to be isoenthalpic.[33,36] However, the differences in heats of transfer of the ion precursors due to differing solute–solvent interactions in the two solvents are expected to be small compared to the substituent effects on the stability of the ions.[36]

It is unfortunate that some of the dihalides are liquids at 25° and solids at −60°. This means that the heat of solution in the acid at −60° must be corrected for the heat of fusion of the dihalide. These experimental data are not available but can be estimated reliably from a plot of heat of fusion *vs.* melting point for a variety of similar compounds.[37] Such a plot is shown in Figure 1. The heats of fusion reported in Table I were estimated using Figure 1.

The heats of formation of the halonium ions from the indicated precursors are given in Table I. Here $\Delta H_{\mathrm{react}}$ is the heat of solution in (and reaction with) the acid at −60°, $\Delta\bar{H}_{\mathrm{S,CCl_4}}$ is the heat of solution in carbon tetrachloride at 25°, $\Delta\bar{H}_{\mathrm{fus}}$ is the heat of fusion, and $\Delta\bar{H}_{\mathrm{obsd}}$ is the heat of transfer from dilute solution in carbon tetrachloride at 25° to the acid at −60°. This last quantity ($\Delta\bar{H}_{\mathrm{obsd}}$) is the heat of formation of the halonium ion (and anion) from the indicated precursor. Since the heat of formation of the anion produced is not known, ΔH_{obsd} is a relative quantity. Differences in ΔH_{obsd} represent differences in the heats of formation of the ions from the indicated precursors in solution provided the leaving group (*i.e.*, the anion formed) remains the same.

One quantity of interest is the thermodynamic stability of the halonium ions compared to other cations. Data allowing this comparison are shown in Table II. The halonium ions are of quite low thermodynamic stability. The more stable bromonium ions have heats of formation close to that of a tertiary carbonium ion and the least stable ion is 10 kcal/mol less stable than this.

The five-membered ring bromonium ions are about 10 kcal/mol more stable than the three-membered ring ions. It is possible to attempt a correction for ring strain using data for the corresponding sulfur compounds. Using the additivity scheme of Benson,[38] the strain energy of a three-membered ring sulfur compound is estimated to be 19.7 kcal/mol and that for a five-membered ring containing sulfur is estimated as 1.7 kcal/mol. Assuming these values will be approximately correct for the bromonium ions, it appears that the three-membered ring bromonium ion is *ca.* 8 kcal/mol more stable than the five when both are corrected for ring strain. This estimate is quite sensitive to the method used to estimate the strain energy. Use of cyclopropane or ethylene oxide as model compounds leads to a value of 18 kcal/mol for the difference in stability between the three- and five-membered ring bromonium ions. We prefer the sulfur compounds as models. In any event,

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[31] Recent work by Arnett[32] as well as studies in our laboratories[33] show quite clearly that the substituent effects on London dispersion interactions of the cation precursor with a solvent makes the use of a solution standard state most convenient.

[32] E. M. Arnett and J. V. Carter, *J. Amer. Chem. Soc.*, **93**, 1516 (1971).

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[34] The reaction generating the halonium ion generates complex anions as well as Br_2 (Paul E. Peterson, personal communication). For our purposes, it is important only that the anionic products be the same, independent of the cation being generated. The substituent effects observed here and in other systems[35] are independent of the leaving group.

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Table I. Heats of Solution ($\Delta \bar{H}_{S,CCl_4}$), Fusion (ΔH_{fus}), and Relative Heats of Formation (ΔH_{obsd}) in 11.5 mol % SbF_5 in FSO_3H at −60° (kcal/mol)

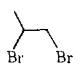
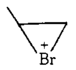
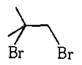
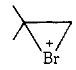
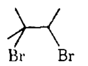
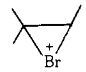
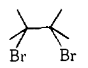
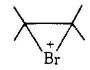
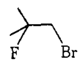
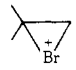
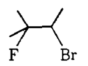
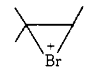
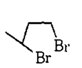
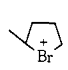
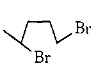
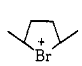
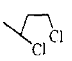
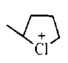
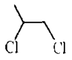
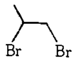
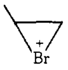
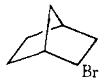
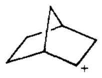
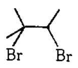
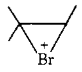
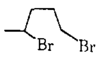
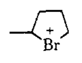
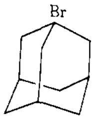
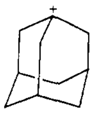
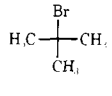
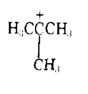
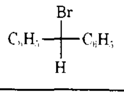
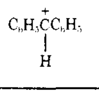
Precursor	Ion	ΔH_{react}	$\Delta \bar{H}_{S,CCl_4}$	ΔH_{fus}	ΔH_{obsd}
		−3.16 ± 0.48	+0.13 ± 0.03		−3.29 ± 0.51
		−8.39 ± 0.87	0.00		−8.39 ± 0.87
		−11.0 ± 0.85	−0.27 ± 0.05	+2.70	−13.4 ± 0.90
		−20.5 ± 3.60	+2.44 ± 0.76		−22.9 ± 4.00
		−10.6 ± 1.80	+0.70 ± 0.03		−11.3 ± 1.83
		−13.3 ± 2.10	+0.21 ± 0.05	+2.00	−15.5 ± 2.15
		−13.5 ± 1.84	+0.33 ± 0.03		−13.8 ± 1.87
		−11.2 ± 1.89	−0.10 ± 0.04	+2.20	−13.3 ± 1.93
		−13.7 ± 0.87	+0.36 ± 0.03		−14.1 ± 0.90
	Polymer	−29.4			

Table II. Heats of Formation of Cations in 11.5 mol % SbF_5 in FSO_3H at −60°

Precursor	Ion	ΔH_{obsd}, kcal/mol
		−3.29 ± 0.51
		−13[a,b]
		−13.4 ± 0.9
		−1.38 ± 1.87
		−14.3 ± 0.20[a]
 $H_3C-\overset{Br}{\underset{CH_3}{C}}-CH_3$	 $H_3C\underset{CH_3}{\overset{+}{C}}CH_3$	−14.5 ± 2.0[a]
 $C_6H_5-\overset{Br}{\underset{H}{C}}-C_6H_5$	 $C_6H_5\underset{H}{\overset{+}{C}}C_6H_5$	−30[a]

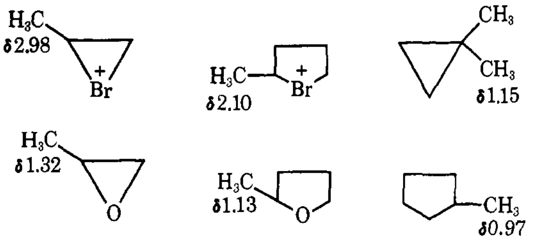
[a] E. M. Arnett and J. W. Larsen, unpublished data. [b] Except for this ion, the nmr spectra of all of these have been observed in this solvent system.

there seems to be extra stabilization in the cyclic three-membered ion.

The stability of the three-membered ring bromonium ion also seems more sensitive to methyl substitution than does the stability of the five. With both bromine and fluorine as the leaving group, substitution of a methyl for a hydrogen results in about a 5-kcal/mol increase in the stability of the ion for all ions except the tetramethylethylene. Calculations indicate that increasing strain in the starting dihalide with increasing methyl substitution is not the source of this effect, the strain energy of 2,3-dibromo-2-methylbutane being only 0.4 kcal/mol. The strain energy in 2,3-dimethyl-2,3-dibromobutene may be enough to explain the large exothermic heat of formation of the tetramethylethylenebromium ion. This would require a larger value for gauche Br–CH_3 interactions than that given by Benson, *et al.*, however.[38] There seems to be no reason to expect extra stabilization of the cation from the fourth methyl group. A better knowledge of the heats of formation of haloalkanes would be helpful in interpreting this value. It is worth noting that if some quite exothermic values for the heat of formation of the ethylenebromonium ion are disregarded, our data suggest a heat of formation of +2 kcal/mol. This is quite consistent with the observed substituent effect. While the errors in the heats of formation of the five-membered ring ions are unfortunately large, it is apparent that the effect of a methyl substituent is considerably reduced. There are many data available which are consistent with an unusually large interaction between a methyl substituent and a three-membered ring. The data most directly comparable to ours have been discussed by Benson.[39] The methyl-substituted thiairanes

are significantly more stable than calculated using additivity rules which work well for other related compounds. This could well be due to increased interaction between the methyl substituent and the three-membered ring. Placing a methyl substituent on ethylene oxide also increases its stability by more than the predicted amount,[38] but in this series the data are much more limited. Winstein has also observed this effect in the solvolysis of some 2-methoxy alkyl tosylates.[40] He discusses this substituent in terms of the "unsaturated" character of the three-membered ring.[41]

While it is quite risky to interpret proton chemical shifts in terms of charge densities, the heats of formation reported here fit quite nicely with the nmr spectra of the ethylene- and tetramethylenebromonium ions. The chemical shifts of the α methyl group in a series of related cyclic compounds are shown below.[42,43] It can be seen that a methyl bound to cyclopropyl is shifted downfield by δ 0.18 when compared with methyl bound to cyclopentyl. This difference is much larger in the bromonium ions, δ 0.88. This is consistent with a greater dispersal of charge to the methyl group bound to the three-membered ring ion concomitant with greater stabilization of this ion by a methyl substituent. It would be desirable to examine this substituent effect in detail using MO calculations.



Comparison of the stabilities of a chloronium and bromonium ion is interesting. This comparison would be more certain if more data for chloronium ions were available. Since the leaving groups involved in the formation of the chloronium and bromonium ions shown in Table I differ, a correction must be made for this. The difference between the heats of formation of the *tert*-butyl cation from *tert*-butyl chloride and bromide is 7.8 kcal/mol.[44] Using this value, the heat of formation of the 1-methyltetramethylenechloronium ion is calculated to be -6.3 kcal/mol with bromide as the leaving group. This is 7.5 kcal/mol less stable than the analogous bromonium ion. The lower stability of the chloronium ion intermediates in solvolysis reactions has been demonstrated.[3,4]

Overall, the picture of the thermodynamic stabilities of the halonium ions considered here is much the same as that which has been inferred from kinetic measurements. The data suggest a particularly favorable interaction between a methyl substituent and a three-membered ring exists, and it is desirable to gather more data bearing on this interaction. MO calculations would be very helpful as would more heats of formation for compounds containing alkyl-substituted three-membered rings.

Experimental Section

The calorimeter and techniques have been described previously.[36] The calorimeter was checked by measuring the heats of solution of potassium chloride and ethanol in water at 25° using a 2000 ohm Veeco 32A1 thermistor in place of the Teflon-coated thermistor used at low temperatures. Our results were within experimental error of the literature values.[45,46] Values for the heats of protonation of several different compounds in 11.5 mol % SbF_5 in FSO_3H previously reported by Arnett and coworkers were also successfully reproduced. A new method of sample introduction was used in this work. A sample was weighed into and sealed in a fragile bulb blown at the bottom of a 15-cm length of 5 mm OD tubing. This tube has a 40° bend 3 cm from the bottom and was held in the calorimeter by a Teflon sleeve near the top. After thermal equilibration, the bulb was broken against the heater coil.

All samples for nmr study were prepared by introducing the sample into 3-4 ml of a rapidly stirred solution of 11.5 mol % SbF_5 in FSO_3H in a 10-ml Erlenmeyer flask cooled in a Dry Ice-acetone bath. All operations were carried out in a dry nitrogen atmosphere. The cold acid solution was rapidly transferred to an nmr tube in a Dry Ice-acetone bath and the spectrum was obtained at $-60°$ with a Varian HA-100 spectrometer. The tetramethylammonium ion was used as the internal standard.

Except for the indicated substances, all compounds were commercially available. Fluorosulfonic acid and antimony pentafluoride were purified by distillation in a dry nitrogen atmosphere. All other compounds were carefully distilled through a Teflon spinning band column. The middle fraction was collected and used soon after distillation. All dihalides gave only one peak when chromatographed on an SE-30 column. Both the nmr and ir spectra showed no evidence of any impurities.

2-Fluoro-2-methyl-3-bromobutane. An attempted synthesis using the reaction of silver fluoride with the dibromide[23] failed. A fluorobromination procedure proved successful.[47] A pint Teflon bottle was flushed with dry nitrogen and 44.5 g of recrystallized *N*-bromosuccinimide and 100 ml of dry ether were added. This mixture was cooled in a Dry Ice-acetone bath and 40 g of anhydrous HF was condensed in the stirred mixture. A solution of 150 g of 2-methyl-2-butene in 20 ml of dry ether was added in 30 min. The reaction mixture was then stirred for 5 hr in the Dry Ice bath and then for 1 hr in an ice bath. After standing overnight in a Dry Ice-acetone bath, the reaction mixture was added to a slurry of 150 g of Na_2CO_3, 100 g of ice, and 150 ml of ether. The layers were separated, the aqueous layer was extracted with two 100-ml portions of ether, and the ether fractions were combined, washed with aqueous Na_2CO_3, and water, and dried with $MgSO_4$. Concentration of the ether followed by distillation gave the desired product in 15% yield: bp 51-52° (65 mm); $n^{22}{}_{D}$ 1.4400.

1-Bromo-2-fluoro-2-methylpropane. The fluorobromination procedure described above was used. Starting with 14 g of isobutylene, 5.2 g (15% yield) of the desired product was obtained.

1,4-Dichloropentane. To a stirred mixture of 43 g of tetrahydrofuran and 1 g of $ZnCl_2$, 70 g of thionyl chloride was added during 80 min while the temperature rose to 82°. The reaction mixture

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(39) Reference 38, pp 308-309.

(40) S. Winstein, C. R. Lindegren, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 75, 154 (1953).

(41) S. Winstein and E. Grunwald, *ibid.*, 70, 828 (1948).

(42) Sadtler Standard Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1969.

(43) JEOL High Resolution NMR Spectra, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1969.

(44) E. M. Arnett and J. W. Larsen, unpublished data.

(45) S. Sunner and I. Wadso, *Acta Chem. Scand.*, **13**, 97 (1959).

(46) E. M. Arnett, W. B. Kover, and J. V. Cater, *J. Amer. Chem. Soc.*, 91, 4028 (1969).

(47) F. H. Dean, J. H. Amin, and F. L. M. Pattison, *Org. Syn.*, **46**, 10 (1966).

was then heated at 130° for 2 hr. The crude product was distilled from the reaction mixture in 90% yield using an aspirator. Distillation using a spinning band column gave a sample: bp 165° (740 mm); $n^{22}\mathrm{D}$ 1.4531 (lit.[48] bp 58–60° (15 mm), $n^{22}\mathrm{D}$ 1.4503).

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[48] H. B. Hass and H. C. Huffman, *J. Amer. Chem. Soc.*, **63**, 1233 (1941).

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The authors are grateful to Professors George Olah and Paul Peterson for the communication of pertinent results in advance of their publication.

The Thermal Decomposition of Substituted 1,2-Dioxetanes. A Consideration of Mechanism

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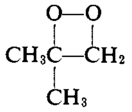
Contribution from the Department of Chemistry, San Diego State College,
San Diego, California 92115. Received May 24, 1971

Abstract: Kinetic data for the thermal decomposition of the cyclic peroxides, 3,3-dimethyl-1,2-dioxetane (**1**) and 3-methyl-3-phenyl-1,2-dioxetane (**2**), in carbon tetrachloride solution are reported. First-order dependence is indicated and the observed activation parameters for **1** and **2** are: $E_a = 23.0 \pm 0.1$ kcal/mol, $\log A = 12.2$ and $E_a = 22.9 \pm 0.2$ kcal/mol, $\log A = 12.1$, respectively. The similarity of activation parameters for **1** and **2** is consistent with a two-step decomposition mechanism. Calculated activation parameters, based on this mechanism, are in reasonable agreement with the observed values. In further support of the two-step mechanism, the reported rate coefficients for alkoxy-substituted 1,2-dioxetanes can be estimated and also show good agreement with those observed. It appears that the previously calculated activation parameters for methyl-substituted 1,2-dioxetanes will serve to estimate kinetic data for diversely substituted 1,2-dioxetanes.

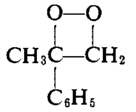
Thermal decomposition of 1,2-dioxetanes is a particularly fascinating reaction, since the ground-state cyclic peroxide produces a carbonyl-containing molecule in an excited singlet state.[1] Preliminary reports of this reaction to effect "photochemistry without light" have been made.[2] The reaction is also of importance to certain biological systems, where bioluminescence is thought to originate from the decomposition of 1,2-dioxetanes.[3]

We have reported some reactions of 1,2-dioxetanes,[4] but the simplest reaction, unimolecular thermal decomposition, is not well understood. Either a concerted process or a two-step mechanism may be operative. Calculations based on orbital symmetry considerations have been made for the concerted process by Kearns and coworkers[5] and we have made thermochemical kinetic[6] calculations based on the two-step mechanism.[7] We now report an experimental test of the two-step mechanism by a study of the thermal decomposition kinetics of 3,3-dimethyl-1,2-dioxetane (**1**) and 3-methyl-3-phenyl-1,2-dioxetane (**2**) in carbon tetrachloride.



$$\mathrm{CH_3\underset{CH_3}{\overset{O-}{C}}-\overset{O}{C}H_2}$$

1



$$\mathrm{CH_3\underset{C_6H_5}{\overset{O-}{C}}-\overset{O}{C}H_2}$$

2

According to the two-step mechanism, resonance interactions by substituents are ruled out, while these effects could influence the rate of the concerted mechanism where π-carbonyl character may be developed in the activated complex.

Results

Preparation of 1,2-Dioxetanes. The preparation and characterization of **1** was reported previously.[4b] Treatment of 1-bromo-2-phenyl-2-hydroperoxypropane with methanolic base at 0° for a limited reaction period, followed by carbon tetrachloride extraction, gave **2** in 15% yield.[8] Unreacted hydroperoxide was removed by base extraction. The nmr spectrum showed the methyl and methylene protons to be in the correct ratio for **2**. A presumed contaminant, 1,2-dibromo-3-phenylpropane, which was believed to be formed in the preparation of the hydroperoxide, did not allow a comparison of the phenyl proton ratio. This contaminant remained unchanged throughout the decomposition of **2**. The concentration of **2** in the carbon tetrachloride solution was determined by nmr methods and checked iodometrically,[9] which indicates that the

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[1] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, 47, 709 (1969).

[2] (a) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, 91, 5194 (1969); (b) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, 92, 2167 (1970).

[3] *Cf.* W. D. McElroy, H. H. Seliger, and E. H. White, *Photochem. Photobiol.*, 10, 153 (1969).

[4] (a) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 749 (1971); (b) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, 93, 3996 (1971); (c) W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, 35, 1216 (1970); (d) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 2271 (1970); (e) W. H. Richardson, J. W. Peters, and W. P. Konopka, *ibid.*, 5531 (1966).

[5] (a) D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, 10, 193 (1969); (b) D. R. Kearns, *J. Amer. Chem. Soc.*, 91, 6554 (1969).

[6] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[7] H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, 92, 6553 (1970).

[8] The preparation of 2 was reported in a communication[2b] by a somewhat different method, but without experimental detail or physical properties.

[9] W. H. Richardson, *J. Amer. Chem. Soc.*, 87, 247 (1965).