in the aromatic region). This product (1 ml) was treated with 4 ml of ethyl bromide in a sealed tube at 130° for 19 hr. After cooling, the contents of the tube were neutralized with aqueous sodium hydroxide and extracted with ether. The ether extract was dried with magnesium sulfate. Glc showed three components, two with retention times identical with those obtained from the photolysis of decyl bromide and diethylaniline. The mixture was chromatographed on acid-washed alumina with Skellysolve H as the eluent. The major component had an nmr spectrum with an AA'BB' quartet centered at δ 6.65 (4, J = 9 Hz), 3.25 (q, 4, J = 8 Hz), 2.4 (m, 2), 1.2–0.9 (m, 25).

Anal. Calcd for $C_{20}H_{35}N$: C, 83.0; H, 12.1. Found: C, 83.4; H, 11.9.

Photolysis of *n*-BuI, *n*-BuBr and *n*-BuCl with Dimethylaniline.—Solutions of *n*-BuI, *n*-BuBr, and *n*-BuCl in benzene were prepared such that these contained 0.01 mol of halide, 0.03 mol of DMA, and 1.5 ml of toluene and the total volume was 10 ml. These solutions were irradiated for 96 hr. The progress of the reaction was followed by nmr, and it was shown that 27% of *n*-BuBr, 12% of *n*-BuCl, and 10% of *n*-BuI had reacted.

Quantum Yields.—The following solutions were prepared: benzophenone (0.91 g) and benzhydrol (0.92 g) in benzene (50 ml); DDT (1.41 g) and diethylaniline (1.2 g) in methanol (net volume 100 ml); and decyl bromide (1.105 g), diethylaniline (1.49 g) and dodecanol (1 ml) in methanol (total volume 25 ml). The uv spectrum of the benzophenone and benzhydrol solution was recorded by diluting 0.5 ml of this solution to 10 ml with benzene. Two 5-ml aliquots and two 7-ml aliquots of this solution were taken in identical Pyrex tubes with long stems. These tubes were degassed by three freeze–thaw cycles to 0.005 mm and sealed *in vacuo*. Three 5-ml aliquots of the DDT solution were taken in Pyrex tubes which were similar to the actinometer tubes. These were photolyzed with two actinometer tubes containing 5 ml of solution for 5 min. The amount of DDT reacted was determined by glc on column 1 at 240° using triphenylmethane as an internal standard which was added after irradiation. The per cent of DDT lost in three tubes was 12.24, 12.2, and 12.4. The per cent benzophenone reacted was determined by recording the uv spectrum of the irradiated solution after diluting 0.5 ml of this solution to 10 ml; the percentage lost was 7.5 and 7.5. The quantum yields were calculated for disappearance of DDT as 0.30, 0.30, and 0.31. Two 7-ml aliquots of the decyl bromide solution prepared above were placed in Pyrex tubes. These were irradiated along with two actinometer tubes (containing 7 ml of solution) for 30 min. The loss of benzophenone was determined as 23.5% in both tubes and of decyl bromide by glc, which was 6.3 and 6.5%. Quantum yields for the reaction were 0.19 and 0.20.

Registry No.—*cis*-**3**, 36954-66-2; *trans*-**3**, 36954-67-3; **5**, 36955-24-5; DDT, 50-29-3; diethylaniline, 91-66-7; decyl bromide, 112-29-8; α,α-bis(*p*-chlorophenyl)-*p*-diethylaminoacetophenone, 36955-25-6; 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-diethylaminophenyl)ethylene, 36955-26-7; *p*-decyl-*N*,*N*-diethylaniline, 36955-27-8; *o*-decyl-*N*,*N*-diethylaniline, 36955-28-9.

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The Free-Radical Bromination of Bromobutane with Bromotrichloromethane

J. H. HARGIS

Department of Chemistry, Auburn University, Auburn, Alabama 36830

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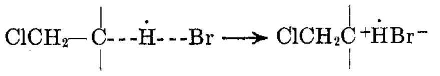
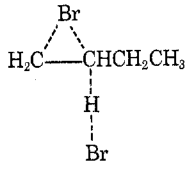
The photolytic bromination of 1-bromobutane with bromotrichloromethane was studied at three different temperatures. Product ratios were observed to be independent of per cent conversion with products resulting from β-hydrogen abstraction predominating. This result is discussed in terms of the stabilization of the β radical by a bromo substituent. A rearrangement product, 2-bromobutane, was also observed and a 1,2 bromine migration in the radical intermediate is proposed to account for its formation.

A large amount of work has dealt with the selectivities of hydrogen atom abstraction from hydrocarbons.[1] Some of the more interesting observations have resulted from studies in which alkyl halides serve as the hydrogen donor.[2–8] These systems are complicated by the effects of the halogen, which could potentially either stabilize or destabilize nearby radical centers. Studies of the photolytic bromination of alkyl chlorides with bromine have shown that a position β to the chlorine substituent is deactivated toward hydrogen abstraction.[3,4] This has been attributed to the polar effect of the electronegative substituent. The electronegative bromine atom is apparently repelled by the decreased electron density adjacent to the chlorine. This can be explained by including in the transition state for hydrogen abstraction an appropriate resonance structure showing some polar contribution to the radical reaction.



$$ClCH_2—\overset{|}{\underset{|}{C}}\text{- - -}\dot{H}\text{- - -}Br \longrightarrow ClCH_2\overset{|}{\underset{|}{C}}{}^{+}\dot{H}Br^{-}$$

A more complicated situation obtains in alkyl bromides. If 1-bromobutane is photolytically brominated using Br_2 as the halogen source, 1,2-dibromobutane is the predominant product.[4] The polar effect has apparently been superseded by a stronger stabilizing influence of the bromo substitutent. Many authors have attributed this effect to a bridged radical species in which the neighboring bromine can anchimerically assist hydrogen abstraction from a β position.[3–9] This bridged radical intermediate postulation is supported by the observed retention of optical activity when optically active 1-bromo-2-methylbutane is halogenated under the same conditions.[9]



An alternative explanation has recently been pro-

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[1] J. M. Tedder, *Quart. Rev., Chem. Soc.*, **14**, 338 (1960).

[2] M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, 1430 (1955).

[3] (a) P. S. Fredericks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960); (b) *ibid.*, 3520 (1961).

[4] W. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963).

[5] P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

[6] P. S. Juneja and E. M. Hodnett, *ibid.*, **89**, 5685 (1967).

[7] P. S. Skell, R. G. Allen, and N. D. Gilmour, *ibid.*, **83**, 504 (1961).

[8] J. G. Traynham and W. G. Hines, *ibid.*, **90**, 5208 (1968).

[9] P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

posed by Tanner and coworkers.[10] These authors have reported that at low conversions, 1,3- rather than 1,2-dibromobutane predominates. This observation is interpreted on the basis of a reversible reaction in which the radical formed by abstraction of a β or γ hydrogen by a bromine atom may subsequently react with HBr to regenerate starting material. The observed product ratios thus are dependent not on the kinetics of hydrogen abstraction but rather on the relative stabilities of the radical intermediates. This interpretation is supported by the demonstration that the product ratio varies as a function of HBr concentration.

We have examined the bromination of 1-bromobutane using bromotrichloromethane with photolytic initiation. It was anticipated that under these conditions large concentrations of HBr would not be formed; thus the reaction could be examined in the absence of this complicating factor.

Results

Degassed solutions containing approximately 8.5:1 ratios of 1-bromobutane to bromotrichloromethane were sealed in Vycor tubes and irradiated for varying lengths of time with a sun lamp at three different temperatures. At completion of the photolyses the products were determined using gas chromatography. Product retention times were compared with those of authentic samples and the detector response was calibrated using known mixtures. The products observed are shown in eq 1 and tabulated in Table I.

$$\mathrm{Br(CH_2)_4H} + \mathrm{BrCCl_3} \xrightarrow{h\nu} \mathrm{CHCl_3} + \mathrm{CH_3CHBr(CH_2)_2H} + \mathrm{BrCH_2CHBr(CH_2)_2H} + \mathrm{Br(CH_2)_2CHBrCH_3} \quad (1)$$

Small amounts of an approximately equimolar mixture of the diastereomeric 2,3-dibromobutanes (0.9, 1.4, and 4.3% of consumed $\mathrm{BrCCl_3}$ at 0, 20 and 40°, respectively) were also formed. The absence of 1,1-dibromobutane was demonstrated by an independent synthesis[11] of this material and noting the lack of a corresponding signal in gas chromatograms of product mixtures.

To establish quantitatively the HBr formed in these reactions, 20° photolysis mixtures corresponding to 5.0 and 11.1% reaction were titrated with base. The titrations allow HBr concentrations of 3.8×10^{-3} and $5.5 \times 10^{-3}\,M$, respectively, to be calculated.

A control reaction showed that 1,2- and 1,3-dibromobutane as well as 1-bromobutane are photostable under our conditions. A 3:1 ratio of 1,2- to 1,3-dibromobutane dissolved in 1-bromobutane was unchanged after 24-hr photolysis at 20°.

An effort to detect 1-butene from the reaction mixture was made by photolyzing ~5 ml of solution at 35° with a medium-pressure Hg lamp while flushing with $\mathrm{N_2}$ and trapping effluent in a liquid air cooled trap. No detectable butenes were formed when the reaction was allowed to proceed to *ca.* 20% completion. In addition no products corresponding to those from a photolytically initiated addition of $\mathrm{BrCCl_3}$ to 1-butene at 20° could be detected in our reaction mixtures.

TABLE I
PRODUCTS[a] OF REACTION OF 1-BROMOBUTANE WITH BROMOTRICHLOROMETHANE

Temp, °C	% R[b]	$\mathrm{CHCl_3}$	2BrBu	$\mathrm{BrCCl_3}$	1,2-BrBu	1,3-$\mathrm{Br_2Bu}$
40[c]	0	0.01	0.03	8.80		
	19.3	1.78	1.11	7.10	0.59	0.42
	23.4	2.39	1.36	6.74	0.73	0.52
	35.6	3.12	1.84	5.66	0.92	0.72
	36.7	3.53	1.73	5.58	0.99	0.73
	51.0	4.27	1.91	4.48	1.26	0.85
	87.0	6.40	2.34	2.02	1.82	1.13
20[c]	0	0.01	0.03	8.80		
	10.3	0.87	0.26	7.88	0.29	0.13
	22.6	1.87	0.52	6.80	0.65	0.32
	27.0	2.62	0.63	6.43	0.96	0.43
	40.5	3.69	0.64	5.24	1.48	0.70
	48.7	4.23	0.89	4.52	1.51	0.72
	63.2	5.30	0.99	3.23	2.12	0.94
0[d]	0	0.02	0.03	8.50		
	2.2	0.23	0.05	8.32	0.13	0.03
	6.4	0.73	0.08	7.96	0.41	0.08
	13.2	0.92	0.09	7.38	0.53	0.13
	54.2	4.55	0.42	3.90	2.53	0.71
0[c]	0	0.01	0.03	8.80		
	4.8	0.46	0.10	8.39	0.19	0.05
	7.0	0.71	0.09	8.17	0.34	0.06
	14.0	1.42	0.16	7.57	0.65	0.20
	26.0	2.58	0.21	6.51	1.34	0.38

[a] μmol of product in sample with PhCl standard normalized to 0.736 mol. [b] Based on consumption of $\mathrm{BrCCl_3}$. [c] 70.66 μmol of 1-bromobutane originally. [d] 62.80 μmol of 1-bromobutane originally.

Discussion

The C–H bond of chloroform and the H–Br bond have similar dissociation energies (90 and 87 kcal/mol, respectively).[12] The ρ values observed in Br· and $\mathrm{CCl_3}$· abstraction reactions from substituted toluenes (-1.36[13] and -1.46,[14] respectively) indicate that these radicals also have similar polar characteristics. These parallel properties allow an interesting comparison of the selectivities of hydrogen atom abstraction from 1-bromobutane to be made. The predominant bromination product in each case is 1,2-dibromobutane. There are, however, significant differences. In contrast to the observations of Tanner, *et al.*,[10a] on the $\mathrm{Br_2}$ system, the 1,2- to 1,3-dibromobutane product ratios (1,2-$\mathrm{Br_2Bu}$/1,3-$\mathrm{Br_2Bu}$) remain essentially constant over a large range of conversions.[15] Figure 1 is a plot of 1,2-$\mathrm{Br_2Bu}$/1,3-$\mathrm{Br_2Bu}$ *vs.* per cent conversion at three temperatures. The large scatter of points from the 0° experiments is probably due to an inability to precisely control the temperature in our crude reactor vessel at significantly subambient temperatures. For comparison Tanner's data of $\mathrm{Br_2}$ bromination at 30° are included in Figure 1.

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(10) (a) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *ibid.*, **91**, 7398 (1969); (b) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, **93**, 4802 (1971); (c) D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971).

(11) J. C. Conly, *ibid.*, **75**, 1148 (1953).

(12) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 48–50.

(13) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 3142 (1963).

(14) E. S. Huyser, *ibid.*, **82**, 394 (1960).

(15) Since completion of this work two groups of workers have reported being unable to duplicate the large variation of dibromobutane ratios with per cent conversion: P. S. Skell and K. J. Shea, *ibid.*, **94**, 6550 (1972), and J. G. Traynham, E. E. Green, Y. Lee, F. Schweinsberg, and C. Low, *ibid.*, **94**, 6552 (1972).

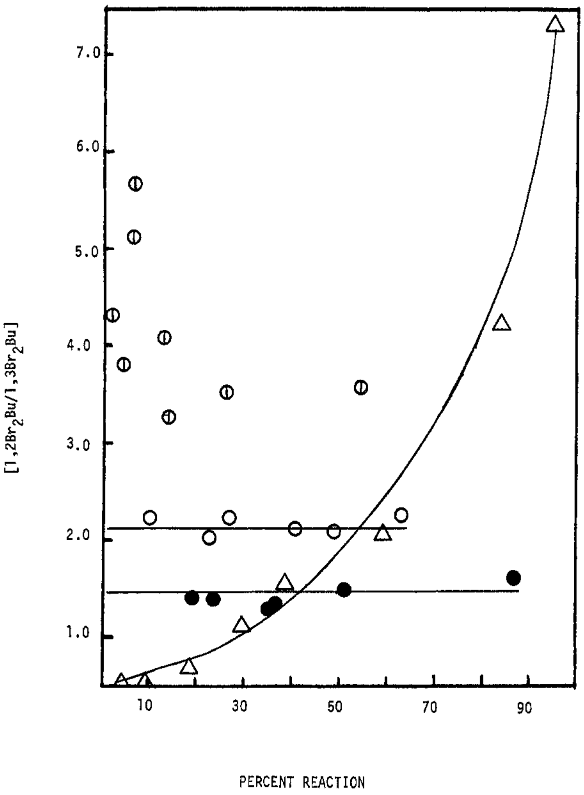


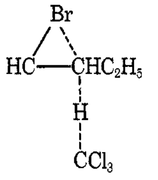
Figure 1.—Ratio of 1,2-dibromobutane to 1,3-dibromobutane as a function of per cent reaction: ⦶, 0°; ○, 20°; ●, 40°; △, Br_2 bromination at 30°.[10a]

We observe consistent predominance of the β abstraction product. We interpret this data to indicate that β-hydrogen abstraction is kinetically favored over γ abstraction. Although we do observe acid formation (6–9% of consumed $BrCCl_3$), the demonstration that the product ratio remains constant while the acid concentration increases argues against HBr allowing reversible formation of bromoalkyl radicals and a thermodynamically controlled product ratio. It is possible that extremely small concentrations of HBr could catalyze the thermodynamic equilibration of the β and γ radicals and thus increasing amounts of HBr would not further affect the observed product ratios. If this were the case, one would expect the ratio of products to be independent of the abstracting species and at least equal to or greater than those observed in the Br_2 system (7.3) as equilibrium is being approached at high HBr concentrations. Since our observed ratios fall far short of this value even when the amount of rearrangement product, which presumably results from β-hydrogen abstraction (*vide infra*), is included (3.46 at 20°), we conclude that the smaller amounts of HBr present in our system are not large enough to allow thermodynamic control to obtain.

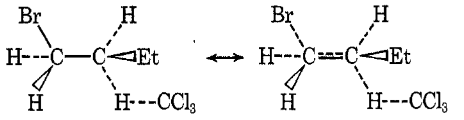
We could be observing thermodynamically controlled products if the bromoalkyl radicals originally formed were being equilibrated *via* chain transfer with starting material before reaction with $BrCCl_3$. The argument above concerning the independence of abstracting species and equilibrium ratios must also be invoked here. On the basis of these arguments and the expected rapid rate of chain transfer with $BrCCl_3$[16] we regard this mechanism for equilibration as a remote possibility.

We must also consider the possibility that the presence of chloroform could result in equilibration. The large difference in reactivity of $CHCl_3$ relative to $BrCCl_3$[16] and the invariance of product ratios when the chloroform concentration has increased argue against this possibility.

The observation of preferential β-hydrogen abstraction by the electronegative trichloromethyl radical[14] necessitates the participation of the bromine substituent in an activating manner rather than the deactivation predicted on the basis of electronic arguments alone. Three possible explanations could be invoked: (1) anchimeric assistance of hydrogen atom abstraction *via* formation of a bromine bridged radical, I; (2) a hyperconjugative delocalization of electron density to bromine *via* a preferred conformation, II; or (3) some type of elimination–addition mechanism proceeding through an intermediate alkene.



I

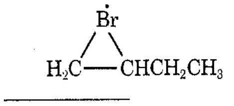


II

Since efforts to trap alkene or detect the addition products of $BrCCl_3$ to 1-butene proved futile, we regard the third possibility as unlikely. Although we cannot definitely distinguish between possibilities 1 and 2, our recent demonstration using CIDNP[17] that the ground-state configuration of the β-bromoethyl radical cannot be the symmetrical bridged structure as well as recent esr data[18] causes us to favor case 2. It is noteworthy that either case 1 or 2 by providing an energetically favored configuration for radical formation would favor the retained product configurations observed using optically active substrates in the Br_2 system.[9,10b]

We also observed formation of a rearrangement product, 2-bromobutane, which has not been reported in the Br_2 system. The most logical mode of formation of this product is *via* bromine atom migration in the β-radical intermediate followed by hydrogen abstraction (eq 2) or abstraction of hydrogen by a bridged radical species (eq 3). A possible alternative route would involve the mechanism proposed by Martin and Williams[19] to explain the γ-radiation induced isomerization of 1-bromobutane to 2-bromobutane. An originally formed β radical could lose Br· to form 1-butene, which can add HBr after the double-bond migration takes place through an allylic radical intermediate. Alternatively, the original alkene

$$BrCH_2\dot{C}HCH_2CH_3 \rightleftarrows \cdot CH_2CHBrCH_2CH_3 \xrightarrow{XH} CH_3CHBrCH_2CH_3 + X\cdot \quad (2)$$



$$\xrightarrow{XH} CH_3CHBrCH_2CH_3 + X\cdot \quad (3)$$

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[16] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 250–253.

[17] J. H. Hargis and P. B. Shevlin, submitted for publication.

[18] A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

[19] D. H. Martin and F. Williams, *ibid.*, **92**, 769 (1970).

could add HBr ionically to form product directly. The inability to gain evidence for alkenes again argues against this mechanism. In addition separate isotopic labeling studies by Tanner[10b] and Ronneau, *et al.*,[20] have failed to provide evidence for "free" alkene intermediates in brominations of 1-bromobutane. 1,2-Bromine atom migrations in free radicals have been previously reported[5–8] usually when a more stable radical is being produced. Traynham,[8] however, has reported products corresponding to a 1,2-bromine migration from a primary to a tertiary carbon.

The failure to note 2-bromobutane from the Br_2 bromination reactions may be due to the decreased rate of chain transfer of $BrCCl_3$ relative to Br_2, but the observation of 10% radiolabeled bromine in the 2 position of 1,2-dibromobutane produced when ^{82}Br 1-bromobutane is brominated with isotopically normal Br_2 suggests that a similar migration is operative in this system.

The observation of the 2-bromobutane product, which must result from β-hydrogen abstraction, is indicative that the ratio of β to γ hydrogen abstraction may be higher than the value obtained from the relative yields of the dibromination products.

The formation of small amounts of *meso*- and *dl*-2-3-dibromobutane is also explicable on the basis of the rearrangement product. A bromotrichloromethane bromination of 2-bromobutane produced these compounds in the same ratio observed in the 1-bromobutane system (~50:50).

Another major difference in the two modes of bromination is the absence of 1,1-dibromobutane formation in the $BrCCl_3$ system while it is a significant product from the Br_2 reaction. This may be due to an unfavorable dipole–dipole interaction between the chlorines of the near-planar $CCl_3\cdot$[21] and the substrate bromine in the transition state for α-hydrogen abstraction.

Experimental Section

With the exception of 1,1-dibromobutane, all chemicals were commercial products. 1,1-Dibromobutane was synthesized by the method of Conly[11] and identified on the basis of its nmr spectrum (CCl_4), δ 0.98 (distorted t, 3), 1.51 (m, 2), 2.40 (m, 2), 5.75 (t, 1). Purification of 1-bromobutane was accomplished by the method of Tanner.[10] All other materials were used without further purification.

Photolyses.—Small portions of approximately 8.5:1 molar ratios of 1-bromobutane to bromotrichloromethane with chlorobenzene added as internal standard were placed in Vycor tubes, degassed by three freeze–thaw cycles, and sealed under vacuum. These tubes were placed in a larger Vycor tube and an ethylene glycol–water mixture from a thermostated bath was pumped through to regulate the reaction temperature.

Photolyses were conducted for various lengths of time with a 275-W G. E. sun lamp. Products were quantitatively determined with a 12 ft × 0.25 in. 20% SE-30 on Chromosorb W glpc column (80° column temperature with 30 ml/min carrier gas flow). The detector response was calibrated using known mixtures. Results are tabulated in Table I.

Titration Experiment.—Solutions containing 2.00 ml of reaction mixture were photolyzed at 20°. The tubes were opened and a 10.0-μl sample was analyzed by glpc. The remaining solution was immediately washed into a flask with a water–isopropyl alcohol mixture and titrated with 0.001 *M* NaOH to a phenolphthalein end point.

Registry No.—1-Bromobutane, 109-65-9; bromotrichloromethane, 75-62-7; 2-bromobutane, 78-76-2.

Acknowledgment.—We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[20] C. Ronneau, J. P. Soumillion, P. Dejaifve, and A. Bruylants, *Tetrahedron Lett.*, 317 (1972).

[21] C. Hesse and N. Leray, *Mol. Phys.*, **22**, 137 (1971).

Anomalous Hydrogen Exchange Reactions in HSO_3F–SbF_5

G. M. KRAMER*

Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036

R. J. PANCIROV

Analytical and Information Division, Esso Research and Engineering Company, Linden, New Jersey 07036

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Olefins, when added to SbF_5–HSO_3F solutions in the presence of alkylcycloalkanes or alkanes, are converted into the corresponding paraffin. However, labeling studies using tritiated acid and methylcyclohexane-d_{14} show that significant amounts of product do not arise *via* a normal carbonium ion path, which would have introduced one proton from the acid and one from the hydride donor into the products. Instead, much of the product appears to form by a process in which the alkylcycloalkane transfers two hydrogen atoms to the olefin. The possibility of a chain reaction at the acid–hydrocarbon interface or the intervention of radical cations leading to these results is considered.

Solutions of antimony pentafluoride in fluorosulfonic acid and other solvents are commonly used for the study of carbonium ions. Much of this work is due to enthusiasm with which Olah and coworkers have explored the field.[1] Recently, a study has been done of the behavior of alkyl cations in the SbF_5–tritiated HSO_3F system wherein the ions were formed by solvolysis of halides and trapped by hydride transfer to yield kinetically controlled products.[2] There it was shown that during many rearrangements a species which contained a very loosely bound and hence exchangeable proton formed. The species could be considered as a protonated alkylcyclopropane inter-

[1] (a) G. A. Olah, Abstracts of the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, p 45; (b) G. A. Olah, W. S. Tolgyesi, J. S. McIntyre, I. J. Bastion, M. W. Meyer and E. B. Baker, Abstract A, 19th International Congress of Pure and Applied Chemistry, London, June 1963, p 121; (c) G. A. Olah and J. A. Olah, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 715.

[2] G. M. Kramer, *J. Amer. Chem. Soc.*, **92**, 4344 (1970).