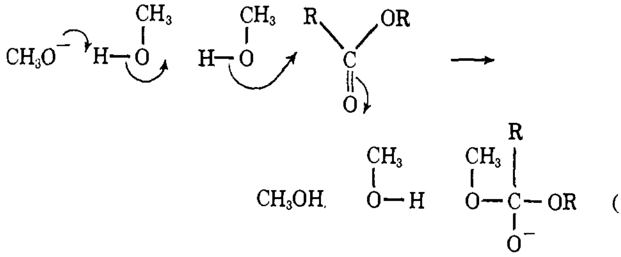
behavior of the aminolysis reaction in methanol at −78.2° is very similar to that of analogous reactions in water at temperatures over 100° higher. On the other hand, the simple kinetics of the low-temperature aminolysis contrasts markedly with those of the aminolysis of esters in ethanol at room temperature which involves terms second and three-halves order in amine.[6]

Reactions of carboxylic acid derivatives in water for which the solvent isotope effect is much greater than unity, as found for the methoxide ion–*p*-NPA system at −78.2°, are well known. Bender and Homer[7] found that in the alkaline hydrolysis of *p*-nitrophenyl N-methylcarbamate $k_{D_2O}/k_{H_2O} = 1.8$, and concluded that the substrate is involved in a solvent-dependent preequilibrium. Bruice and co-workers[8] attributed the large ratio for the alkaline hydrolysis of 2,2-dichloroethyl acetate to the difference in nucleophilicity of OH^- and OD^-. Clearly neither type of rationale is applicable to the methoxide–*p*-NPA reaction at low temperature because the substrate is nonionizable and the nucleophile is identical in the normal and heavy methanol. The isotope effect for the reaction of methoxide with phenyl benzoate in methanol at 25.0° is smaller than 2.6 but still sizeable ($k_{MeOD}/k_{MeOH} = 1.9$),[3] showing that low temperature is not necessary for a ratio greater than unity. Differences in solvating properties[9] of methanol and methanol-*d* must be sufficient to cause the large effects.

The reaction of methoxide ion with *p*-NPA in methanol may involve (A) no intervening reacting solvent molecules or (B) one or more of them (eq 1). Proton transfer in water is associated with a large isotope effect ($k_{D_2O}/k_{H_2O} \ll 1$),[10] pointing to a nonclassical behavior of the proton. The k_{MeOD}/k_{MeOH} ratio for the methoxide–*p*-NPA reaction would also be expected to be much less than unity if mechanism B applied, particularly if proton tunnelling were important at the reduced temperature. The observation that the ratio is in fact greater than unity (2.6) indicates that mechanism B is incorrect. Desolvation, or partial desolvation, of the nucleophile must be an integral part of the mechanism. Even at the low temperature, where it is more difficult to break solvation bonds, "long-range" reactivity of the methoxide is not present. Clearly in the case of *n*-butylaminolysis of *p*-NPA at −78.2° a Grotthuss-like mechanism is not operating through the solvation shell of the amine because little methyl acetate is formed.[11]


(1)

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(6) J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **82**, 665 (1960).

(7) M. L. Bender and R. B. Homer, *J. Org. Chem.*, **30**, 3975 (1965).

(8) T. C. Bruice, T. H. Fife, J. J. Bruno, and P. Benkovic, *J. Am. Chem. Soc.*, **84**, 3012 (1962).

(9) R. E. Robertson and P. M. Laughton, *Can. J. Chem.*, **35**, 1319 (1957); C. A. Bunton and V. J. Shiner, *J. Am. Chem. Soc.*, **83**, 3207, 3214 (1961).

(10) M. Eigen, *Angew. Chem. Intern. Ed. Engl.*, **3**, 1 (1964).

(11) A more detailed analysis and a description of further experiments in this area are forthcoming.

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F. M. Menger
Department of Chemistry, Emory University
Atlanta, Georgia

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The Intermediacy of Protonated Cyclopropanes in the Addition of Bromine to Cyclopropane

Sir:

Baird and Aboderin reported that addition of D_2SO_4 to cyclopropane in 57% D_2SO_4 produced monodeuterated 1-propanol and monodeuterated 1-propyl hydrogen sulfate with deuterium on C-1, C-2, and C-3.[1] It was reasoned that other addition reactions of cyclopropane should show similar complexity.

The addition of Br_2 to cyclopropane has now been examined, and 1,1-dibromopropane, 1,2-dibromopropane, and 1,3-dibromopropane are all produced. The results are presented in Table I.

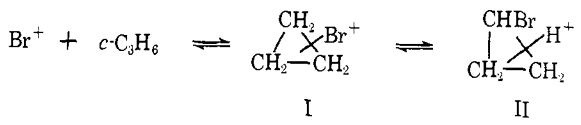
Table I. Products from the Reaction of Br_2 and Cyclopropane

			% yields based on Br			
Temp, °C	Time, hr	Catalyst (g/100 g of Br_2)	Dibromopropanes 1,1	1,2	1,3	CH_3-CHBr-$CHBr_2$[a]
−15	12	Fe (1)	[b]	46	39	2.5
60	1	Fe (1)	[b]	60	10	12
65	0.25	$AlCl_3$ (6.7)	~5	~5	30	12
25	240[c]	$AlBr_3$ (0.5)	3.8	2.8	15	3

[a] The pmr spectrum consisted of a doublet (J = 6.5 cps) at δ 1.90, a complex multiplet at 4.3–4.7, and a doublet at 5.96 (J = 3 cps). This is definitive along with the boiling point of 200–201° (G. B. Bachman, *J. Am. Chem. Soc.*, **57**, 1090 (1935); B. K. Mereshkowsky, *Ann.*, **431**, 239 (1923)). The yield was computed on the basis that the gc band area had the same proportionality to weight as the dibromopropanes using a thermal conductivity detector. [b] The 1,1-dibromopropane is unstable under the reaction conditions. However, it does not produce the isomeric dibromopropanes on decomposition. The 1,2 and 1,3 isomers are stable. [c] The reaction was largely incomplete.

The production of all three dibromopropanes is interpreted to be the result of equilibration between intermediate protonated monobromocyclopropanes, c-$C_3H_6Br^+$. The interpretation parallels the equilibration of intermediate isomeric c-$C_3H_6D^+$ species, which were proposed by Baird and Aboderin to rationalize the deuterium scrambling in the addition of D_2SO_4 to cyclopropane.[1]

$$Br_2 + FeBr_3 \rightleftharpoons Br^+FeBr_4^-$$



$$\text{I} + Br^- \longrightarrow \text{1,3-dibromopropane}$$

$$\text{II} + Br^- \longrightarrow \text{1,1-dibromopropane and 1,2-dibromopropane}$$

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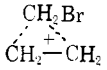
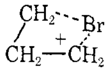
(1) R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964). This result has been confirmed with minor revision in 57% D_2SO_4 and throughout the 57–96% D_2SO_4 range. Also confirmed was the report that monodeuteriocyclopropane was formed (A. A. Aboderin and R. L. Baird, *Tetrahedron Letters*, 235 (1963)), and this result has now been extended to 57–96% D_2SO_4.

A noncommittal representation has been used for I and II. Using I for an example, either bridged (III) or edge-attached (IV) geometries are attractive. At present, there is little basis for choice and they may interconvert so rapidly that the distinction loses importance. Baird and Aboderin invoked both forms and felt that this was necessary on the basis that unequal amounts of deuterium were found on C-1 and C-2 in the 1-propyl derivatives. Their argument does not seem acceptable in view of the magnitude of kinetic isotope effects,[2] and furthermore, in our work on D_2SO_4 plus cyclopropane (the details to be published later), equal amounts of deuterium were found on C-1 and C-2.


III


IV

The three dibromopropanes were identified by gas chromatography (gc) retention times and by proton magnetic resonance (pmr) spectra of samples isolated by preparative gc. Authentic samples were used for comparison in both types of observations.[3]

The additions of Br_2 to cyclopropane is presented in texts as typifying additions to cyclopropane, and the product is given as 1,3-dibromopropane. In the light of the data in Table I, it is of interest to examine the basis for this presentation. Gustavson[4] could not separate the dibromopropanes produced. On the basis that the mixture gave both propene and cyclopropane on treatment with Zn dust, Gustavson concluded that both 1,2- and 1,3-dibromopropanes had been present.

The addition of Br_2 to cyclopropane at 25° under irradiation has been variously reported (1) to react slowly and give unidentified products[5] and (2) to produce 1,3-dibromopropane.[6] The latter report based the identification on refractive index and density, which is unsatisfactory. Curiously, Cl_2 plus cyclopropane at $-30°$ in the presence of 1% $FeCl_3$ gave over 90% 1,3-dichlorocyclopropane.

One other example of 1,2 addition to cyclopropane existed at the time of this work. It had been found that acetylation of cyclopropane produced products of 1,2 and 1,3 addition with the 1,2-addition product dominating in the ratio 2:1.[7] Recently, Hart and Schlosberg have reinvestigated this reaction and found up to 10% of the 1,1-addition product under certain conditions.[8] They have interpreted these results in terms of intermediate protonated cyclopropanes, and our interpretations parallel theirs.

One other aspect of the presentation in texts is misleading. In the addition of Br_2 to cyclopropane no catalyst is indicated, whereas in the bromination of benzene $FeBr_3$ is usually placed above the arrow, indicating that it is required. We have found that $FeBr_3$ is needed even more for the cyclopropane reaction than for the benzene reaction.[9] In a competition experiment between benzene and cyclopropane at $-12°$, using 1% $FeBr_3$ as a catalyst (introduced as Fe + Br_2) and a deficiency of Br_2, the products were entirely bromobenzene and bromopropane (from HBr + cyclopropane). It is concluded that cyclopropane is much less reactive toward Br^+ than is benzene.

Acknowledgment. We are grateful to the National Science Foundation for a grant to support the purchase of the Varian A-60 nmr spectrometer and a fellowship for D. N. L.

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(2) The closest analogy is the effect of α-deuteration on carbonium ions where the calculated k_H/k_D for an isolated carbonium ion is 1.4 and the observed S_N1 solvolysis rates average around 1.15 (A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 173).

(3) The 1,1-dibromopropane was made by treatment of α-bromobutyramide with Br_2 in aqueous alkali (C. L. Stevens, T. K. Mukerjee, and V. J. Traynelis, *J. Am. Chem. Soc.*, **78**, 2264 (1956). The other two isomers were commercially available.

(4) G. Gustavson, *J. Prakt. Chem.*, [2] **62**, 273 (1900), and earlier papers.

(5) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939).

(6) R. A. Ogg, Jr., and W. J. Priest, *ibid.*, **60**, 217 (1938).

(7) H. Hart and O. E. Curtis, Jr., *ibid.*, **79**, 931 (1957); H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1267 (1959).

(8) H. Hart and R. H. Schlosberg, submitted for publication.

(9) Gustavson[4] reported that concentrated aqueous HBr catalyzed the addition of Br_2 to cyclopropane. In our hands, it was without effect.

N. C. Deno, David N. Lincoln
Department of Chemistry, Pennsylvania State University
University Park, Pennsylvania 16802

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Anisole in Sulfuric and Fluorosulfuric Acid

Sir:

The position of protonation of anisole is of theoretical interest and practical importance in the use of anisole or similar compounds as Hammett bases. It is well established[1,2] that anisole in $HF-BF_3$ or SbF_5-FSO_3H is protonated predominately on the *p*-carbon. Ultraviolet spectral evidence has been interpreted to suggest that in aqueous H_2SO_4 anisole protonates predominately on oxygen.[3]

A recent communication[4] suggested that solvents which promote hydrogen bonding will favor protonation of anisole on oxygen, and that in concentrated sulfuric acid one may observe a change from C to O protonation. While reasonable and relevant in comparison of aqueous acids with systems such as $HF-BF_3$, the proposal unfortunately centers around an incorrect assignment to *para*-protonated anisole of the 284- and 240-mμ bands which appear in the ultraviolet spectrum of anisole in concentrated H_2SO_4. The λ_{max} 284 mμ band has been assigned by Birchall and Gillespie[1a] to *para*-protonated anisole, whereas in fact the spectrum observed in concentrated H_2SO_4 must be attributed to sulfonated anisole.

We have found the text of ref 1b on the nmr spectrum of anisole in FSO_3H to be misleading. The text and presentation of spectra indicate at room temperature a CH_3 resonance at $\delta = 4.8$ ppm relative to external TMS, with the appearance of a new CH_2 resonance at 4.4 ppm when the sample is cooled below 0°. Examination of the published room temperature spectrum, using the published scale, indicates the CH_3 resonance at 4.4 ppm, *not at 4.8 ppm.*

We have found that the nmr spectra of anisole in FSO_3H and concentrated H_2SO_4 are substantially the

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(1) (a) T. Birchall, A. Bourns, R. Gillespie, and B. Smith, *Can. J. Chem.*, **42**, 1433 (1964); (b) T. Birchall and R. Gillespie, *ibid.*, **42**, 503 (1964).

(2) D. M. Bronwer, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim.*, **85**, 109 (1966).

(3) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 5660 (1960).

(4) A. J. Kesege and L. E. Hakka, *ibid.*, **88**, 3868 (1966).