[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Stereochemistry of the Primary Carbon. II. Esters of Optically Active Butanol-1-*d*. Solvolysis of Butyl-1-*d* Brosylate[1]

BY ANDREW STREITWIESER, JR.

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Chemical purity of optically active butanol-1-*d* is demonstrated by the constancy of rotation of its hydrogen phthalate ester during repeated recrystallization and by its regeneration from this ester with unchanged rotation. Optically active butyl-1-*d* acetate and formate are described. The solvolysis of butyl-1-*d* *p*-bromobenzenesulfonate in acetic acid and in formic acid goes with inversion of configuration accompanied by little if any racemization. These results are discussed in terms of the modern concepts of the solvolysis reaction.

It was demonstrated recently that the reduction of butyraldehyde with optically active 2-octyl-2-*d*-oxymagnesium halide in ether is partially stereospecific, the butanol-1-*d* resulting having a small optical rotation.[2] The probable reality of this optical activity was demonstrated by the application of several criteria of purity. This purity has now been established further by working with a solid derivative.

The butanol-1-*d* prepared in run W had, after two distillations through a small column, $[\alpha]^{25}_{\mathrm{D}}$ $-0.032 \pm 0.002°$, $[\alpha]^{25}_{5461}$ $-0.044 \pm 0.002°$. One portion of this material was distilled through another small column, a center cut having $[\alpha]^{25}_{\mathrm{D}}$ $-0.036 \pm 0.002°$, $[\alpha]^{25}_{5461}$ $-0.044 \pm 0.002°$, the constancy of the rotation demonstrating homogeneity toward distillation. The remainder of the butanol-1-*d* was converted to the crystalline hydrogen phthalate with phthalic anhydride and pyridine. After two, four and six recrystallizations from benzene–hexane this material had, respectively, $[\alpha]^{25}_{\mathrm{D}}$ $+0.070 \pm 0.004°$, $+0.067 \pm 0.005°$ and $+0.073 \pm 0.005°$ (*c* 25, acetone). The rotation is unchanged within experimental error. The homogeneity of the product was demonstrated further by saponification. Alkaline hydrolysis of the combined last four mother liquors generated butanol-1-*d* having $[\alpha]^{25}_{\mathrm{D}}$ $-0.036 \pm 0.002°$, $[\alpha]^{25}_{5461}$ $-0.046 \pm 0.002°$, differing insignificantly from the starting alcohol and from that regenerated by the alkaline hydrolysis of the recrystallized ester which had $[\alpha]^{25}_{\mathrm{D}}$ $-0.036 \pm 0.002°$, $[\alpha]^{25}_{5461}$ $-0.045 \pm 0.002°$. It should be noted that the use of two wave lengths provides two independent determinations of rotatory power and gives further meaning to the results obtained. There can now be little doubt of the reality of the rotation found for butanol-1-*d*.

A portion of this (−)butanol-1-*d* was converted to (+)butyl-1-*d* acetate with acetyl chloride and pyridine. This ester had $[\alpha]^{25}_{\mathrm{D}}$ $+0.094 \pm 0.001°$, $[\alpha]^{25}_{5461}$ $+0.111 \pm 0.001°$. Alkaline hydrolysis regenerated butanol-1-*d* with $[\alpha]_{\mathrm{D}}$ $-0.033 \pm 0.009°$. Since the preparation of both esters involved reactions not expected to affect the asymmetric center, the over-all retention of configuration in the cycle means that the alkaline hydrolysis of the esters also did not affect the asymmetric center. This stereochemical result for a primary aliphatic alcohol is well known for secondary aliphatic systems and complements the results obtained by the use of heavy oxygen.[3]

A sample of the alcohol was also converted to (+)butyl-1-*d* formate by refluxing with formic acid. The formate obtained had $[\alpha]^{25}_{\mathrm{D}}$ $+0.121 \pm 0.002°$, $[\alpha]^{25}_{5461}$ $+0.147 \pm 0.005°$. It is interesting to note that all three esters have signs of rotation opposite that of butanol-1-*d* of related configuration. By contrast, most secondary aliphatic alcohols yield esters having the same sign of rotation.[4] The limited data available for tertiary alcohols preclude any generalization.[5]

It is noteworthy that the dispersion ratio, $\alpha_{5461}/\alpha_{\mathrm{D}}$, for butanol-1-*d*, 1.23 ± 0.02, is only slightly higher than the values, 1.16–1.18, found for aliphatic secondary alcohols[6] and the value 1.168 found for methylethylisobutylcarbinol, the only tertiary alcohol for which the ratio is known. The dispersion ratios for butyl-1-*d* acetate, 1.18 ± 0.02, and for butyl-1-*d* formate, 1.21 ± 0.04, are quite close to the values, 1.16–1.18, shown by esters of secondary aliphatic alcohols[4] and to the value, 1.164, the inverse ratio of the squares of the wave lengths, expected theoretically in a wave length region far from an optically active absorption band.[7] These limited measurements indicate that the appreciable optical activity arising from hydrogen–deuterium asymmetry shows a normal dependency on wave length.

The reaction of the above (−)butanol-1-*d* with *p*-bromobenzenesulfonyl chloride in pyridine produced (+)butyl-1-*d* *p*-bromobenzenesulfonate (brosylate) in good yield (88%) having $[\alpha]^{25}_{\mathrm{D}}$ $+0.015 \pm 0.003°$, $[\alpha]^{25}_{5461}$ $+0.011 \pm 0.005°$. This material was solvolyzed in acetic acid and in formic acid. In order that the number of half-lives of solvolysis be known, the rates of solvolysis were determined in the two solvents. These rate constants are collected in Table I.

Reaction of this brosylate in acetic acid at 99.4° for 1.22 half-lives gave (−)butyl-1-*d* acetate. The sign of rotation shows that a net inversion of con-

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[1] Presented in part at the 126th Meeting of the American Chemical Society, New York, N. Y., Sept. 13, 1954.

[2] A. Streitwieser, THIS JOURNAL, **75**, 5014 (1953).

[3] M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934); M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

[4] For example, see R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 830 (1914).

[5] 2,4-Dimethylhexanol-4 and its related hydrogen phthalate have opposite signs of rotation [W. E. Doering and H. H. Zeiss, THIS JOURNAL, **72**, 147 (1950)], while 3,7-dimethyloctanol-3 and its corresponding acetate were briefly reported to have the same sign of rotation. Since this material apparently was obtained from a natural product, linaloöl, the significance of this work is open to question. No experimental details were given [C. A. Bunton, E. D. Hughes, C. K. Ingold and D. F. Meigh, *Nature*, **166**, 680 (1950)].

[6] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1923 (1913).

[7] W. Fickett, private communication.

TABLE I

RATE OF SOLVOLYSIS OF BUTYL BROSYLATE

Solvent	Temp., °C.	$10^5 k$, sec.$^{-1}$	$\Delta E^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
Acetic acid	60.0	0.030 ± 0.001	24.1	−18
	99.4	1.43 ± .04		
Formic acid	60.0	0.793 ± .031	19.5	−26
	99.6	18.4 ± .4		

figuration has taken place. The averages of a large number of determinations of rotation, $[\alpha]^{25}\mathrm{D}$ −0.090 ± 0.007°, $[\alpha]^{25}_{5461}$ −0.107 ±0.011°, correspond to 96 ± 8% and 96 ± 9% inversion, respectively. Any racemization which may have occurred in this case was too small to be detected.

Similarly, a further quantity of the brosylate was solvolyzed in dry formic acid at 60° for 1.0 half-lives giving a 50% yield of crude (−)butyl-*d* formate having $[\alpha]^{25}\mathrm{D}$ −0.108°, $[\alpha]^{25}_{5461}$ −0.135°, corresponding, respectively, to 89 and 92% inversion of configuration. It was not possible to purify this material adequately and still have enough for meaningful polarimetry. The presence of any of the solvent pentane would tend to lower the magnitude of the rotation and, consequently, these figures should be taken as minimum values. For this reason, an estimated error cannot be assigned. However, the conclusion from these results that the amount of racemization accompanying formolysis is less than 10% is in agreement with the results of a second formolysis described below which produced close to 0% racemization.

The unreacted brosylate recovered from the formolysis was treated with sodium acetate in methanol. The butyl-1-*d* acetate formed had $[\alpha]^{25}\mathrm{D}$ −0.088 ± 0.002°, $[\alpha]^{25}_{5461}$ −0.112 ± 0.003°, corresponding to 94 ± 3% and 101 ± 5% inversion, respectively. This may be compared to the 100% inversion expected for such a bimolecular displacement reaction.

The butanol-1-*d* used for the second formolysis was obtained from run S and contained only 28 atom per cent. deuterium.[3] It had the correspondingly lower rotation, $[\alpha]\mathrm{D}$ +0.010 ± 0.001°, $[\alpha]_{5461}$ +0.013 ± 0.002°. This rotation remained unchanged by further fractionation. In two separate preparations the butyl-1-*d* formate prepared by refluxing this alcohol with formic acid had $[\alpha]^{25}\mathrm{D}$ −0.030 ± 0.002°, $[\alpha]^{25}_{5461}$ −0.040 ± 0.003° and $[\alpha]\mathrm{D}$ −0.032 ± 0.001°, $[\alpha]^{26}_{5461}$ −0.040 ± 0.002°.

It should be noted that unlike the reaction of alcohols with acid halides and pyridine, the preparation of formate esters by refluxing an alcohol with formic acid could jeopardize the asymmetric center. Kenyon, *et al.*,[10] have found, however, that no racemization is incurred in the preparation of the formates of secondary alcohols by this method and that no change in configuration results. The fact that the butyl-1-*d* formate obtained after 2 and after 24 hours of refluxing in formic acid had the same rotations and the observations which follow demonstrate that for primary alcohols also, the preparation of formates by this procedure does not lead to partial racemization. When the formate was maintained in a dry formic acid solution, 0.2 *M* in *p*-bromobenzenesulfonic acid, for 26.5 hours at 99° (corresponding to 24 half-lives for the formolysis of the brosylate) it was recovered with a rotation of $[\alpha]^{25}\mathrm{D}$ −0.031 ± 0.001°, $[\alpha]^{26}_{5461}$ −0.040 ± 0.002°. The ester, therefore, does not racemize under the solvolysis conditions. This may be contrasted to the relative ease of racemization of a secondary ester, 2-octyl acetate, in acetic acid containing a strong acid.[11]

A sample of the butanol-1-*d* from run S was converted to the brosylate which was solvolyzed in dry formic acid at 99° for 4.3 hours (4.0 half-lives). The butyl-1-*d* formate isolated had $[\alpha]^{25}\mathrm{D}$ +0.031 ± 0.002°, $[\alpha]^{26}_{5461}$ +0.039 ± 0.001°, corresponding to 99 ± 6% and 97 ± 4% inversion, respectively.

Some measure of the reproducibility which could be obtained in separate experiments also is demonstrated by the conversion of butanol-1-*d* from run X having $[\alpha]^{26}\mathrm{D}$ +0.038 ± 0.002°, $[\alpha]^{27}_{5461}$ +0.046 ± 0.002°, to butyl-1-*d* formate having $[\alpha]^{27}\mathrm{D}$ −0.131 ± 0.001°, $[\alpha]^{27}_{5461}$ −0.163 ± 0.002°. The ratios of the rotations of this formate to those of the alcohol, −3.4 ± 0.2 at the sodium D line and −3.5 ± 0.2 at the mercury 5461 Å. line agree quite well with the corresponding ratios obtained for the butanol-1-*d* and its formate obtained from run W, −3.4 ± 0.2 and −3.3 ± 0.2, respectively, and from run S, −3.1 ± 0.3 and −3.1 ± 0.5, respectively.

Discussion

While a considerable amount of work has been done on the mechanism of the solvolysis of primary halides and sulfonate esters from a kinetic standpoint, a stereochemical approach has hitherto been inapplicable although such an approach is capable, in principle, of imposing unique conditions on any proposed reaction mechanism. With the preparation of optically active butanol-1-*d*, the application of stereochemical criteria is made feasible. It should be noted that an attempt to use an optically active butyl-1-*d* halide in this type of experimentation would be expected to invoke several uncertainties; *e.g.*, the relative configurations of an alcohol and the corresponding halide are exceedingly difficult to establish with any degree of certainty[12] and the halide ion produced during the solvolysis of an alkyl halide would be expected to cause more or less facile racemization of the unreacted substrate.[2] These difficulties are avoided by the use of sulfonate esters which manifest reactions quite comparable to those of the halides.[13]

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[8] The 2-octanol-2-*d* used in this preparation was prepared by the reduction of methyl hexyl ketone with sodium and deuteroacetic acid.[2,9] The lability of the α-hydrogens in the ketone resulted in extensive enolization with consequent dilution of the deuterium. It should be noted that the products of runs Q, R-1 and R-2,[2] in which this diluted octanol was also used had about 28 atom per cent. deuterium as measured by the infrared spectra. The large rotation obtained for the samples, unexpected for so low a deuterium content, was found subsequently to be due to some unknown impurity. These samples had not been distilled to constant rotation because of the limited quantities available but point out the necessity for this precaution.

[9] D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, THIS JOURNAL, **74**, 5599 (1952).

[10] R. H. Pickard, J. Kenyon and H. Hunter, *J. Chem. Soc.*, **123**, 1 (1923).

[11] M. P. Balfe, W. H. F. Jackman and J. Kenyon, *ibid.*, 965 (1954).

[12] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *ibid.*, 1252 (1937).

[13] R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

The expected finding that the acetolysis and formolysis of butyl-1-*d* brosylate resulted in a net inversion of configuration is of less significance than the question of the extent of racemization incurred. The fact that these reactions were accompanied by little or no racemization would be consistent with a direct displacement by solvent (an SN2 reaction in the Hughes–Ingold terminology)[14] involving a structure such as I (Fig. 1) as a *transition state.* While there is evidence that such a mechanism is involved in the solvolysis of primary halides in such strongly nucleophilic solvents as ethanol and water,[13,15] relative rate studies indicate that this is not the case for solvents of the low nucleophilicity of acetic and formic acids. For example, bimolecular displacement reactions are some twenty times faster with methyl compounds than with ethyl,[16] presumably because of a difference in steric hindrance. Correspondingly, methyl halides and sulfonates solvolyze 2–3 times as fast as the ethyl esters in alcoholic solvents,[13] but only 10% faster in acetic acid while only about *half* as fast in formic acid.[18] The latter solvolyses cannot be of the direct displacement type without violating the relative rate generalizations established for authentic displacements.[16] If the solvolyses are not of the direct displacement type, the involvement of intermediates may be postulated.

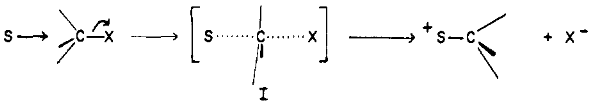

Fig. 1.—Bimolecular displacement mechanism for solvolysis.

All of the kinetic and stereochemical data are quite consistent with a mechanism utilizing intermediates of the type proposed by Doering and Zeiss.[19] In this approach (Fig. 2), the rate-determining step leads to an *intermediate*[20] of structure II, the dotted lines representing bonds to each lobe of the empty p-orbital of the central carbonium ion. Subsequent reactions of this intermediate can occur by rehybridization to form a normal sp^3-bond with the solvent molecule giving the inverted product IV or, alternatively, the leaving brosylate ion can be replaced by a solvent molecule giving the intermediate III, which, being symmetrical, must produce racemic product V. The accommodation of the present stereochemical results is accomplished in this scheme by the plausible postulation of instability of the intermediates II and III. These intermediates are primary carbonium ions "covalently solvated" above and below the plane of the ion. Contrary to the tertiary case reported on by Doering and Zeiss, the inability of the primary carbon to effectively delocalize a positive charge means that intermediate II is very unstable *relative to the solvolysis product IV, having normal bonding; i.e.,* formation of intermediate III cannot compete effectively in this case with the "collapse" of II into IV.

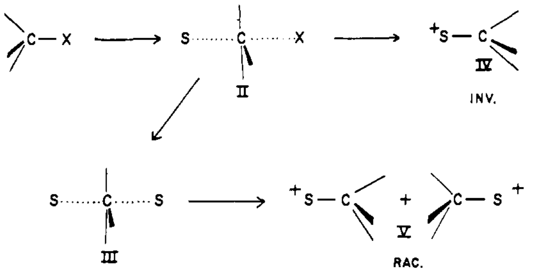

Fig. 2.—Mechanism for solvolysis *via* intermediates of the Doering–Zeiss type.

Since a solvent molecule is explicitly involved in the initial intermediate II, it must be involved also to some degree in the transition state leading to this intermediate, and, therefore, in the kinetics of the process since this is the rate-determining step. The contribution of the solvent to the energetics of the system will depend to a large extent on the length and strength of the carbon–solvent bond at the transition state and these will depend on the electronic requirements of the system itself; *i.e.*, the energy of this bond would be expected to vary over a rather wide range as the solvent and substrate are varied. In the present case of a primary central carbon with its low steric requirements and relative inability to delocalize a positive charge,[21] the carbon–solvent bond at the transition state would be expected to be shorter and stronger than that involved, for example, in the tertiary case considered by Doering and Zeiss. A natural corollary is that the energy of the transition state will depend more markedly on the nucleophilicity of the solvent than in the case of secondary and tertiary systems which can better support a positive charge.[21] It is therefore of interest that $k_{\mathrm{EtOH}}/k_{\mathrm{AcOH}}$ at 75° is 39 for ethyl tosylate[18] but only 3.8 for isopropyl brosylate,[18] while for *t*-butyl chloride at 70° it is only 0.43,[22] acetic acid being far less nucleophilic than ethanol.

Besides utilizing the mechanistic considerations of Doering and Zeiss, the foregoing discussion compares closely with the Winstein[23] treatment of the solvolysis reaction in terms of **N** and **Lim.** mechanisms, the greater detail in pictorialization being justified by the new stereochemical results.[24] It is also

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(14) J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 936 (1935).

(15) M. J. Bird, E. D. Hughes and C. K. Ingold, *ibid.*, 255 (1943).

(16) The rate constants for 29 such reactions can be summarized by the expression log ($k_{\text{ethyl}}/k_{\text{methyl}}$) = −1.33, with a median deviation of 0.43. Similarly, for 31 reactions run on both ethyl and propyl systems, log ($k_{\text{ethyl}}/k_{\text{propyl}}$) = 0.36 with a median deviation 0.08 (unpublished compilation of the author). Similar relationships have been derived for other systems. The work of Swain[17] may be cited as evidence for the generality of such correlations.

(17) C. G. Swain and D. C. Dittmer, THIS JOURNAL, **75**, 4627 (1953).

(18) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

(19) W. E. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953).

(20) See footnote 19 in ref. 19.

(21) A. G. Evans, *Trans. Faraday Soc.*, **42**, 719 (1946).

(22) E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

(23) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

(24) It is pertinent at this point to compare this viewpoint with the SN1 mechanism of Hughes and Ingold[25,26] in view of a recent criticism.[27] In this hypothesis the rate-determining step leads to an intermediate formulated as R^+X^- (where X is the leaving group) which subsequently may react with solvent either at the rear or at the front. Since attack from the front is sterically hindered by the leaving group, a predominance of inversion results. It is difficult to see how this mechanism can explain the negligible racemization observed for the primary case and still be operationally significantly different from an SN2 displacement by solvent. The further postulation[28] of complete ionization when the leaving group has separated by 0.5 Å. more

of interest that since these considerations lead to the conclusion that solvent is intimately associated with the first transition state, the rates of solvolysis should be lower for isobutyl and neopentyl systems in which increased steric requirements would suppress such covalent solvation. Inasmuch as the relative formolysis rates at 75° for ethyl, isobutyl and neopentyl tosylates are, in fact, 1.0, 1.22 and 1.0, respectively,[18] the present stereochemical results offer further evidence for the suggestion of Winstein and Marshall[18] that in the latter cases, an anchimeric[31] rate enhancement appears as a consequence of positive charge delocalization *via* carbon–hydrogen and carbon–carbon bond participation.

Experimental

Optical rotations were taken on a Rudolf precision polarimeter on which readings could be made to the nearest 0.001°. With the exception of butyl-1-*d* hydrogen phthalate which is solid, determinations of rotation were made on the pure liquids. Because of the ease with which subjective influences may affect the determination of optical rotations, especially with the narrow bore (2 mm.) polarimeter tubes used in much of this work, the following technique was adopted to ensure objectivity. At least six to ten readings were taken at each of several positions of the half-shade angle. This had the effect of changing the appearance and character of the field and of giving a measure of independence to each set of readings. Readings of the zero point were taken *after* each set of readings for a given half-shade angle. The determination of the zero point could be made quite precisely and without prejudice. Extensive tests showed that the same zero point was obtained for the empty air path as for tubes of various sizes, empty or filled with racemic liquids. With the small bore tubes used no trouble was encountered by rotations contributed by the end glasses. Reproducibility of rotations under these conditions is thought to constitute a fair measure of objectivity.

Each rotation recorded is the mean of a set of readings with the estimated error given as the average deviation from the mean. The resultant rotation for each compound is given as the average of all the means, the resultant error assigned being determined in the usual way from the individual average deviations. For the large number of determinations made for each rotation, the average deviation is proportional to the probable error and is probably a more realistic measure of the range within which the true rotation lies.

Butanol-1-*d* (Run W).—The yield was improved by a few changes in the original procedure.[2] To the Grignard reagent prepared from 67.5 g. of ethyl bromide and 15.1 g. of magnesium was added with stirring 81.5 g. (0.62 mole) of 2-octanol-2-*d* (prepared by reduction of 2-octanone with lithium aluminum deuteride and resolution) having α^{20}_{D} +3.81° (*l* 0.5). To this mixture stirred in an ice-bath was then added 44.6 g. (0.62 mole) of freshly distilled butyraldehyde followed by dry ether to a total volume of one liter. After four hours at room temperature, dilute hydrochloric acid was added. The separated ether layer was washed successively with dilute hydrochloric acid and water and dried with anhydrous potassium carbonate. The aqueous layers were combined and continuously extracted with ether for two days. After washing and drying, removal of the solvent left a residue which on distillation afforded 2.9 cc. of material, b.p. 95–115°. An equal volume of residue remained which did not distil with a pot temperature > 200° and which was not investigated further. Ether was removed from the main extract and the residue was distilled through a glass-spiral fractionating column collecting 21.7 cc., b.p. 114–116° (total yield 43%). The combined butanol-1-*d* fractions were redistilled through the same column, two large center cuts, b.p. 115–116°, having, respectively, α^{25}_{D} −0.103 ± 0.007°, α^{25}_{5461} −0.147 ± 0.008° (*l* 4) and α^{25}_{D} −0.105 ± 0.005°, α^{25}_{5461} −0.144 ± 0.006° (*l* 4). While the other fractions were used for the preparation of the hydrogen phthalate (below), these two fractions, 12.3 cc., were distilled through a small tantalum wire spiral column, the main cut, b.p. 116–117°, 7.1 cc., having d^{25}_{4} 0.8169, α^{22}_{D} −0.117 ± 0.005°, α^{22}_{5461} −0.143 ± 0.007° (*l* 4).

Hydrogen *n*-Butyl-1-*d* Phthalate.—The remainder of the butanol-1-*d* prepared above, 9.7 cc., was refluxed overnight with 21 g. of phthalic anhydride in 100 cc. of dry pyridine. On pouring into iced dilute hydrochloric acid, the initially oily precipitate solidified. Recrystallization from benzene–hexane gave 18.1 g. of crystals which were recrystallized five more times from the same solvent mixture, the rotation being determined after every other recrystallization. After the second recrystallization, the 14.2 g. of large white prisms had $[\alpha]^{25}_{\mathrm{D}}$ +0.070° (α_{D} +0.069 ± 0.004° (*l* 4), +0.036 ± 0.004° (*l* 2, *c* 25.0, acetone)). After two more recrystallizations the 10.4 g. of white prisms had $[\alpha]^{25}_{\mathrm{D}}$ +0.067° (α_{D} +0.066 ± 0.005° (*l* 4), +0.034 ± 0.005° (*l* 2, *c* 25.0, acetone)). After the sixth recrystallization, 6.4 g. was obtained having $[\alpha]^{25}_{\mathrm{D}}$ +0.073° (α_{D} +0.068 ± 0.008°, (*l* 4), +0.040 ± 0.006° (*l* 2, *c* 25.0, acetone)). The effect of wave length on rotation was measured in more concentrated solution: $[\alpha]^{25}_{\mathrm{D}}$ +0.066°, $[\alpha]^{25}_{5461}$ +0.074° (α_{D} +0.033 ± 0.004°, α_{5461} +0.037 ± 0.006° (*l* 1, *c* 50, acetone)). The acetone solvent was found to have no rotation. The rotation in 95% ethanol: $[\alpha]^{25}_{\mathrm{D}}$ +0.077° (α_{D} +0.069 ± 0.006° (*l* 4), +0.033 ± 0.004° (*l* 2, *c* 22)). These rotations were taken in wide bore (6 mm.) tubes which gave large clear fields that were easy to match.

The recrystallized material was steam distilled from 6 g. of sodium hydroxide in 25 cc. of water. The distillate was extracted three times with pentane. After drying, the pentane was removed and the residue was distilled from a small flask collecting 2.0 cc., b.p. 115–117°, having α^{25}_{D} −0.119 ± 0.007°, −0.119 ± 0.006° (*l* 4), α^{25}_{5461} −0.072 ± 0.006°, −0.076 ± 0.004° (*l* 2), −0.145 ± 0.008° (*l* 4).

The third through sixth mother liquors were evaporated in a stream of dry air and the combined residues, 7.3 g., were hydrolyzed in the same way. The butanol-1-*d* generated was distilled from a small flask collecting 2.3 cc., b.p. 114–116°, having α^{25}_{D} −0.118 ± 0.006°, α^{25}_{5461} −0.151 ± 0.009° (*l* 4), α^{25}_{D} −0.060 ± 0.006°, α^{25}_{5461} −0.074 ± 0.009° (*l* 2).

Butyl-1-*d* Acetate.—While 2.5 cc. of butanol-1-*d* from run W was stirred with 5 cc. of pyridine and 12 cc. of pentane in an ice-bath, 2.5 cc. of acetyl chloride in 5 cc. of pentane was dropped in. After stirring at room temperature for several hours, the mixture was washed with dilute acid and water and then dried. Distillation through a small Vigreux column followed by a second distillation of the center cuts gave 2.2 cc., b.p. 123–125°, having α^{25}_{D} +0.332 ± 0.005°, +0.335 ± 0.006°, α^{25}_{5461} +0.395 ± 0.004° (*l* 4), α^{25}_{D} +0.168 ± 0.005°, α^{25}_{5461} +0.198 ± 0.007° (*l* 2), and d^{25}_{4} 0.8833 (calculated assuming constancy of molar volume: 0.8840). This material again was distilled through a small Vigreux column collecting 1.2 cc. of a center cut, b.p. 123–124°, having α^{25}_{D} +0.160 ± 0.004°, α^{25}_{5461} + 0.192 ± 0.006° (*l* 2), n^{25}_{D} 1.3958. The average rotation is taken as α_{D} +0.331 ± 0.005° (*l* 4) ($[\alpha]_{\mathrm{D}}$ +0.094 ± 0.001°), α^{25}_{5461} +0.392 ± 0.005° (*l* 4) ($[\alpha]_{5461}$ +0.111 ± 0.001°). The

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than its normal bonding distance also may be criticized. Using the tables of Mulliken, *et al.*,[29] the Slator overlap integrals for pσ–pσ-bonds have been evaluated as a function of distance for C–Cl and C–O. The values of the integrals at this separation, 0.21 and 0.17, respectively, correspond to quite appreciable *covalent* bonding. (For comparison, the pπ–pπ-bond in a carbon–carbon double bond has an overlap of 0.25). If there is appreciable bonding energy in the hypothesized intermediate R^+X^-, clearly there must be still more bonding energy in intermediates such as II and III, favoring the existence of the latter structures as reaction intermediates. It is also pertinent to note at this point that it is not at all clear how the reaction model recently elaborated by Hughes and Ingold[30] is to be given modern expression in terms of intermediates and transition states and, therefore, no comment is possible.

(25) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(26) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. VII.

(27) W. A. Waters and P. B. de la Mare in *Ann. Repts. on Prog. Chem.* (*Chem. Soc. London*), **50**, 135 (1953); compare this opinion with that expressed by M. J. S. Dewar, *ibid.*, **48**, 122 (1951).

(28) Reference 25, p. 1006.

(29) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1948).

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infrared spectrum differed little from that of butyl acetate except for a band at 2200 cm.$^{-1}$ assigned to C–D stretching.

Saponification of Butyl-1-*d* Acetate.—The combined butyl-1-*d* acetate fractions (above), 1.8 g., were refluxed with 25 cc. of 1 *N* sodium hydroxide for three hours. After distillation, the product, devoid of any odor of ester, was dissolved in pentane and dried. Distillation afforded 0.65 cc. of butanol-1-*d* having $\alpha^{25}\mathrm{D}$ −0.027 ± 0.007° (*l* 1).

Butyl-1-*d* Formate. From Run W.—Three cubic centimeters of butanol-1-*d* from run W was refluxed with 3.0 cc. of 98% formic acid for 24 hours. After cooling, the mixture was shaken with pentane and water. The pentane solution was washed and dried. The aqueous solutions were extracted again with pentane and this solution, after washing and drying, was combined with the main pentane extract. Two distillations through a small Vigreux column gave 1.2 cc., b.p. 105–105.5°, having $\alpha^{25}\mathrm{D}$ +0.213 ± 0.005°, +0.218 ± 0.007°, +0.218 ± 0.004°, $\alpha^{25}{}_{5461}$ +0.259 ± 0.007°, +0.247 ± 0.005° (*l* 2). The combined fractions containing the formate were redistilled, the center 1.6 cc., b.p. 104–106°, having $\alpha^{26}\mathrm{D}$ 0.217 ± 0.005°, +0.213 ± 0.006°, $\alpha^{26}{}_{5461}$ +0.267 ± 0.007°, +0.276 ± 0.007° (*l* 2). The average rotation is taken as: $\alpha\mathrm{D}$ +0.216 ± 0.003° (*l* 2), ($[\alpha]\mathrm{D}$ +0.121 ± 0.002°, using d^{25} 0.892[32]), α_{5461} +0.262 ± 0.009° (*l* 2), ($[\alpha]_{5461}$ +0.147 ± 0.005°).

From Run X.—The butanol-1-*d* obtained from run X (similar to run W) had, after three distillations, $\alpha^{26}\mathrm{D}$ +0.131 ± 0.008°, +0.120 ± 0.007°, $\alpha^{27}{}_{5461}$ +0.149 ± 0.008°, +0.154 ± 0.006° (*l* 4). Two and five-tenths cubic centimeters of this alcohol was refluxed with 8 cc. of 98% formic acid for 2.5 hours. After cooling, 8 cc. of water was added and the mixture was extracted with pentane. After washing and drying, the pentane solution was distilled yielding 2.0 cc. of the formate, b.p. 103–106°, having $n^{28}\mathrm{D}$ 1.3861, $\alpha^{27}\mathrm{D}$ −0.462 ± 0.006°, −0.469 ± 0.007°, $\alpha^{28}{}_{5461}$ −0.585 ± 0.006°, −0.573 ± 0.006° (*l* 4). Redistilled, a center 1.3 cc., b.p. 105–105.5°, had $\alpha^{27}\mathrm{D}$ −0.238 ± 0.006°, −0.233 ± 0.004°, $\alpha^{27}{}_{5461}$ −0.298 ± 0.007°, −0.298 ± 0.005° (*l* 2), and $n^{28}\mathrm{D}$ 1.3859. The infrared spectrum showed no unusual features, the C–D stretching band occurring at 2207 cm.$^{-1}$.

From Run S.—Three cubic centimeters of butanol-1-*d* from run S (below) was refluxed with 3.0 cc. of 98% formic acid for 24 hours. On cooling, the mixture was poured into water and extracted with pentane. After washing and drying, the pentane solution was distilled through a small Vigreux column, the ester fraction, b.p. 104–107°, 2.2 cc., having $\alpha^{25}\mathrm{D}$ −0.112 ± 0.008°, −0.101 ± 0.010°, $\alpha^{25}{}_{5461}$ −0.141 ± 0.009° (*l* 4). Redistillation of this material gave 1.4 cc. of a center cut, b.p. 104°, having $\alpha^{26}\mathrm{D}$ −0.050 ± 0.004°, $\alpha^{26}{}_{5461}$ −0.064 ± 0.009° (*l* 2), and $n^{28}\mathrm{D}$ 1.3860.

In a second experiment, 8.0 cc. of run S butanol-1-*d* was refluxed with 20 cc. of 98% formic acid for two hours. An equal volume of water was added and the mixture was extracted with pentane. Washing, drying and distilling the pentane solution gave 6.3 cc. of a center fraction, b.p. 104–106°, having $\alpha^{25}\mathrm{D}$ −0.116 ± 0.004°, −0.110 ± 0.004°, $\alpha^{26}{}_{5461}$ −0.140 ± 0.006°, −0.141 ± 0.009° (*l* 4), and $n^{28}\mathrm{D}$ 1.3859.

The average rotation was: $\alpha\mathrm{D}$ −0.110 ± 0.004°, α_{5461} −0.141 ± 0.003 (*l* 4); therefore, $[\alpha]\mathrm{D}$ +0.031 ± 0.001°, $[\alpha]_{5461}$ + 0.040 ± 0.002°. The infrared spectra of both samples were superimposable.

Butyl *p*-Bromobenzenesulfonate.—A mixture of 14.8 g. of butanol and 200 cc. of dry pyridine was cooled in an ice-salt-bath for several minutes before 51.2 g. of *p*-bromobenzenesulfonyl chloride was added. The mixture was stirred magnetically in the cooling bath for one hour, then poured into a mixture of 250 cc. of concentrated hydrochloric acid and 1000 cc. of ice and water. The heavy oil was extracted into 500 cc. of hexane. The dried and filtered hexane solution was cooled in a Dry Ice-bath causing the brosylate to precipitate. This material was filtered and freed from residual hexane by prolonged evacuation at room temperature. The product, 46.5 g. (79.2% yield) of a clear colorless liquid, had a melting point near 0°, and $n^{21}\mathrm{D}$ 1.5333.

Anal.[33] Calcd. for $C_{10}H_{13}O_3SBr$: C, 40.96; H, 4.47; S, 10.94; Br, 27.26. Found: C, 40.94; H, 4.40; S, 10.76; Br, 27.54.

Butyl-2-*d* *p*-Bromobenzenesulfonate.—By the same procedure, using 5.0 cc. of butanol-1-*d* (from run W) and 16.0 g. of *p*-bromobenzenesulfonyl chloride in 45 cc. of pyridine, 14 g. (88% yield) of butyl-1-*d* brosylate was obtained as a faint cloudy oil, $n^{21}\mathrm{D}$ 1.5322. The material was centrifuged before the rotation was determined, but the material was still sufficiently colored to prevent the use of polarimeter tubes greater than 1-dc. in length: $\alpha^{25}\mathrm{D}$ +0.020 ± 0.005°, +0.022 ± 0.002°, α_{5461} +0.021 ± 0.007°, +0.008 ± 0.005° (*l* 1).

Acetolysis of Butyl-1-*d* *p*-Bromobenzenesulfonate.—A 0.2 *M* solution was made up by dissolving 12.8 g. (0.0435 mole) of butyl-1-*d* brosylate (from run W, above) in 220 cc. of dry acetic acid which had been preheated in a thermostat maintained at 99.4 ± 0.1°. The solution was maintained at this temperature for 16.0 hours (1.22 half-lives), then cooled in running water. The solvent and the butyl-1-*d* acetate formed were removed by room temperature lyophilization at 2 mm., the distillates being caught in Dry Ice traps. The residue, a brown oil, was shaken with hexane and water. After drying, the hexane solution was cooled in Dry Ice. The precipitated brosylate was filtered and evacuated for several hours. This recovered material, 5.2 g. (96% of the unreacted brosylate), was used for the formolysis (below).

The lyophilate was poured into water and extracted with pentane. After washing and drying, the pentane solution was distilled giving 2.1 cc. of butyl-1-*d* acetate, b.p. 124–125°, having $\alpha^{25}\mathrm{D}$ −0.178 ± 0.008°, −0.180 ± 0.007°, $\alpha^{25}{}_{5461}$ −0.188 ± 0.004°, −0.151 ± 0.011°, −0.177 ± 0.007°, −0.157 ± 0.007°, −0.181 ± 0.004° (*l* 2). A second set of determinations the following day gave : $\alpha\mathrm{D}$ −0.156 ± 0.004°, −0.166 ± 0.006°, α_{5461} −0.215 ± 0.005°, −0.214 ± 0.008°, −0.220 ± 0.006°. The ester was distilled through a small column, 1.5 cc., b.p. 121°, redistilled, the center 1.3 cc. having $\alpha^{25}\mathrm{D}$ −0.136 ± 0.005°, −0.153 ± 0.009°, −0.146 ± 0.007°, $\alpha^{25}{}_{5461}$ −0.184 ± 0.008°, −0.181 ± 0.006 (*l* 2), and $n^{28}\mathrm{D}$ 1.3916. The unweighted average of almost 200 readings is $\alpha\mathrm{D}$ −0.159 ± 0.013° and α_{5461} −0.189 ± 0.019° (*l* 2), corresponding to 96 ± 8% and 96 ± 9% inversion, respectively. The reproducibility reported here is lower than that usually obtained by the author. The infrared spectrum was identical with that of the butyl-1-*d* acetate described above.

Formolysis of Butyl-1-*d* *p*-Bromobenzenesulfonate at 60°. Butyl-1-*d* brosylate was prepared from 2.4 cc. of butanol-1-*d* (from run W) and 8 g. of *p*-bromobenzenesulfonyl chloride. Evacuation of the hexane solution left 6.35 g. of the brosylate which was combined with material recovered from the acetolysis and dissolved in 200 cc. of dry[18] formic acid. This solution was maintained at 60.0 ± 0.1° for 24 hours (1.0 half-lives), then cooled in ice and extracted with pentane. The formic acid solution was then lyophilized. From the residue, 5.3 g. (92% of unreacted brosylate) of butyl-1-*d* brosylate was recovered. The lyophilate was diluted with water and extracted with pentane. The combined pentane extracts were washed and dried. Distillation through a small Vigreux column gave 1.2 cc., collected over the range 78–103°. This material had $\alpha^{25}\mathrm{D}$ −0.185 ±0.008°, −0.196 ± 0.005°, −0.192 ± 0.005°, $\alpha^{25}{}_{5461}$ −0.240 ± 0.005°, −0.239 ± 0.007° (*l* 2), $\alpha\mathrm{D}$ −0.097 ± 0.006° (*l* 1). If this product is considered to be pure butyl-1-*d* formate, the rotations correspond to 89 ± 3% and 92 ± 4% inversion, respectively. The infrared spectrum was the same as that given by the butyl-1-*d* formate from run X. It would be difficult to detect a small amount of pentane impurity by infrared spectroscopy.

Displacement of Butyl-1-*d* *p*-Bromobenzenesulfonate with Acetate Ion.—The butyl-1-*d* brosylate recovered from the formolysis (above), 5.3 g., was dissolved in 30 cc. of reagent grade methanol and refluxed for 0.5 hour with 5 g. of fused sodium acetate. By the end of the reflux period, the flask was filled with white plates. The mixture was shaken with water and extracted with pentane. The pentane solution was washed, dried and distilled, yielding 1 cc. of butyl-1-*d* acetate having $\alpha^{25}\mathrm{D}$ −0.160 ± 0.004°, −0.155 ± 0.004°, −0.152 ± 0.004°, $\alpha^{25}{}_{5461}$ −0.200 ± 0.010°, −0.196 ± 0.006° (*l* 2). The average rotation is taken as: $\alpha\mathrm{D}$ −0.156 ± 0.003°, α_{5461} −0.198 ± 0.005° (*l* 2), corresponding to 94 ± 3% and 101 ± 5% inversion, respectively.

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(32) This value for the density was calculated from the density of butyl formate extrapolated from the data of T. Hannotte [*Bull. soc. chim. Belg.*, **35**, 90 (1926)].

(33) Analysis by the Microanalytical Laboratory of the University of California.

Butanol-1-*d* (from Run S).—This preparation was conducted in much the same way as that of run W, using 15.1 g. of magnesium, 67.5 g. of ethyl bromide, 81.0 g. of the 2-octanol-2-*d* prepared earlier[2] by the reduction of octanone-2 with sodium and deuteroacetic acid, having α_D −3.41° (*l* 0.5), and 44.6 g. of freshly distilled butyraldehyde. After two distillations through small columns a fraction, b.p. 117°, had d^{25}_4 0.8089 and α_D +0.026 ± 0.006° (*l* 4). Repeat determinations at a later date gave α^{24}_D +0.032 ± 0.004°, α^{24}_{5461} +0.041 ± 0.005°. On refractionation, a center cut had α^{25}_D +0.025 ± 0.005°, α^{25}_{5461} +0.038 ± 0.004°. The yield was 18.1 g. (39%).

The density corresponds to 26 atom per cent. deuterium while the several infrared spectra taken at various times gave the values 26, 28 and 29%.

Formolysis of Butyl-1-*d* *p*-Bromobenzenesulfonate at 99°.—Butyl-1-*d* brosylate was prepared from 4.33 cc. of butanol-1-*d* from run S in the usual way. The 13.9 g. (88%) obtained in this way was maintained at 0.3 mm. for several hours at room temperature and for several minutes on the steam-bath to remove any traces of residual hexane or unreacted butanol. It then was dissolved in 200 cc. of preheated anhydrous formic acid and maintained at 99.0 ± 0.1° for 4.3 hours (4.0 half-lives). After cooling in ice and diluting with an equal volume of water, the mixture was extracted with pentane. The washed and dried pentane extracts were distilled, yielding 2.1 cc. of butyl-1-*d* formate, b.p. 104–106° and n^{28}_D 1.3859, having α^{25}_D +0.109 ± 0.007°, +0.109 ± 0.008°, α^{26}_{5461} +0.134 ± 0.005°, +0.140 ± 0.007°, indicating 99 ± 6% and 97 ± 4% inversion, respectively.

Optical Stability of Butyl-1-*d* Formate to Acid.—Five cubic centimeters of butyl-1-*d* formate prepared from run S butanol-1-*d* (above) and 10.6 g. of *p*-bromobenzenesulfonic acid (dried in a vacuum oven overnight) was dissolved in 223 cc. of dry formic acid and maintained at 98.7 ± 0.1° for 26.5 hours. After cooling in ice and diluting with water, the mixture was extracted with pentane. After washing and drying, distillation of the pentane extract gave 2.1 g. of recovered ester, b.p. 104–106°, having α^{25}_D −0.106 ± 0.005°, −0.114 ± 0.008°, α^{26}_{5461} −0.141 ± 0.010°, −0.139 ± 0.008°, and n^{28}_D 1.3859.

Kinetic Measurements.—For the acetolysis rates 0.1 *M* solutions of the butyl brosylate were made up with anhydrous acetic acid. Aliquots were placed in individual flasks which were tightly stoppered and placed in a thermostat. At intervals, a flask was withdrawn and its contents titrated with a 0.1 *M* solution of potassium acetate in acetic acid to a brom phenol blue end-point (yellow). For the formolysis rates, a solution 0.1 *M* in the brosylate was made up with dried formic acid.[18] This solution in a flask containing a condenser and drying tube was placed in the thermostat, zero time being taken when temperature equilibration was reached, at which point and at intervals thereafter a sample was removed and cooled to room temperature. Five cc. was then pipetted, diluted with 50 cc. of dry acetic acid and titrated potentiometrically with potassium acetate in acetic acid. The method used is quite similar to that described by Winstein[18] with the exception that the titrations were made using as electrodes a glass electrode and a silver chloride coated platinum wire, a Beckman *p*H meter being used as the potentiometer. By this method *p*-toluenesulfonic acid monohydrate in a mixture of acetic and formic acids (10:1) titrated to a neutralization equivalent of 192.2 (calculated 190.2). When titrated in acetic acid to a brom phenol blue end-point, the equivalent weight was 192.0. The results of the four runs made are recorded in Table I, the data for one run being given in Table II.

TABLE II

FORMOLYSIS OF BUTYL BROSYLATE AT 60.0 ± 0.1°

Time, sec.	Titer	$10^5 k$, sec.$^{-1}$
0	0.015	...
11890	(.47)	0.815
21150	.763	.774
35600	1.200	.755
79950	2.334	.769
95600	2.673	.778
180000	3.938	.826
268500	4.585	.860
∞	5.100	...
	Average	0.793 ± 0.031

2,4-Dimethylhexanol-4.—A sample of the alcohol[5] which had α^{25}_D −3.71 (*l* 2) had α^{25}_{5461} −4.34 (*l* 2), hence the ratio α_{5461}/α_D is 1.168.

BERKELEY 4, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Anion Exchange of Triphenylmethyl Chloride in Benzene Solution[1,2,3]

BY C. GARDNER SWAIN AND MAURICE M. KREEVOY[4]

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First-, second- or third-order kinetics was observed for anion exchange of triphenylmethyl (trityl) chloride with quaternary ammonium salts at 50° in homogeneous benzene solution: first order with radiochloride or fluoride (rate independent of salt concentration); second order with radiochloride and phenol (rate proportional to phenol) or with azide ion (rate proportional to salt); and third order with azide and phenol. The first-order reactions must involve a rate-determining ionization of trityl chloride aided by only the benzene. The third-order reaction must be a concerted displacement. The kinetic order reflects whether zero, one or two solute molecules have replaced benzene in solvating transition state partial charges. A competition experiment which has been done with fluoride and radiochloride in benzene solution proves the existence of a capturable intermediate.

Organic halides generally require both nucleophilic and electrophilic solvation in the transition state in order to react. Benzene is a solvent of low, but by no means negligible, nucleophilic and electrophilic solvating power. If all solvation is done by benzene, first-order kinetics must be observed. If solutes replace benzene in neither, either or both of these kinds of solvation, the kinetic order is generally first, second or third, respectively.[5]

First-order kinetics has not been observed previously for a reaction of an organic halide in such a weakly polar solvent as benzene. In the present study first-order kinetics was observed in the exchange of triphenylmethyl (trityl) chloride with a

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[1] Abstracts of 125th A.C.S. Meeting, Kansas City, Missouri, March 23–April 1, 1954, p. 22N.

[2] For further details see M. M. Kreevoy, Ph.D. thesis, M.I.T., September, 1953.

[3] Supported in part by the program of research of the Atomic Energy Commission.

[4] Moore Fellow, 1952–1953.

[5] Lower orders are possible with polyfunctional reagents (*cf.* C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2538 (1952)); higher orders occur at high concentrations (*e.g.*, above 0.2 *M* methanol, where more than one methanol molecule may be involved in electrophilic solvation).