Electrolyte Effects upon Acid-Catalyzed Ester Hydrolyses[1]

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Abstract: For the hydrolysis of methyl mesitoate (following the $A_{Ac}1$ mechanism) and *t*-butyl acetate and benzoate (following the $A_{Al}1$ mechanism), the catalytic order of strong acids is $HClO_4 > H_2SO_4 > HCl$, whereas for $A_{Ac}2$ hydrolyses of methyl benzoate and ethyl acetate it is $H_2SO_4 \sim HCl > HClO_4$, with $HCl \sim HBr$ for the hydrolysis of ethyl acetate. Consistently, perchlorates have a greater salt effect than chlorides upon the acid hydrolysis of *t*-butyl acetate, whereas the opposite is true for that of ethyl acetate. Apparently the lower the charge density of an anion the more it stabilizes those transition states which have carbonium ion character, whereas the opposite is found for A2 reactions, where there is considerable hydrogen bonding between the solvent and the transition state. The effect of salts upon the stability of the tri-*p*-anisylmethyl cation relative to that of the *p*-nitroanilinium ion is $NaClO_4 > LiClO_4 > CH_3SO_3Na > NaBr > NaNO_3 > NaCl > LiCl$, showing that the salt order for these equilibria also depends upon the nature of the anions.

Acid-catalyzed hydrolyses are usually classified in terms of the molecularity of the rate-limiting step, and various tests have been proposed to differentiate between A2 mechanisms in which a water molecule is covalently involved in the transition state and A1 reactions in which bond breaking occurs before attack of water.[2] For A1 reactions the rate approximately follows Hammett's acidity function, and for A2 reactions it sometimes follows the hydrogen ion concentration,[3] but generally there is no precise relation between rate and acid concentration or protonating power, and the Zucker–Hammett hypothesis is no longer regarded as a reliable test of mechanism. Many workers have therefore introduced the order with respect to water activity as a kinetic parameter,[4–6] or have used a rate equation involving both hydrogen ion concentration and protonating power.[7]

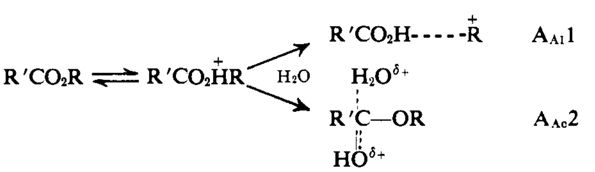
Although there are many kinetic studies of hydrolyses in moderately concentrated acid, they generally relate to only one strong acid. Long and his co-workers have shown that added salts have specific kinetic effects upon some acid-catalyzed hydrolyses,[8] which often can be related to the salt effect upon the activity coefficient of the substrate; *e.g.*, in the acid-catalyzed hydrolysis of γ-butyrolactone, which follows the $A_{Ac}2$ mechanism, added sodium chloride increased the hydrolysis rate and sodium perchlorate decreased it, paralleling their effects on the activity coefficients of the lactone.[8a]

Our interest in this aspect of the acid hydrolysis of carboxylic esters was stimulated by the observation that sulfuric and hydrochloric acids are more effective catalysts than is perchloric acid in those hydrolyses of carboxylic anhydrides which have the A2 mechanism,[9] in part because of stabilization of the anhydride by perchlorates, as compared with chlorides or sulfate[9,10] (*cf.* ref 8a).

The available evidence suggested that hydrolyses of esters and related compounds which involved nucleophilic attack of a water molecule upon an acyl center (by mechanisms $B_{Ac}2$ or $A_{Ac}2$) were retarded by anions of low charge density, such as perchlorate, but were hindered only slightly, or even assisted, by anions of high charge density, such as sulfate or chloride. On the other hand, perchlorates have large positive salt effects upon SN1 solvolyses, even in polar hydroxylic solvents, and perchloric acid is a more effective catalyst than sulfuric acid in the hydrolysis of methyl mesitoate, which follows an $A_{Ac}1$ mechanism.[11]

Therefore we have explored the possibility that strong acids having anions of high charge density would be the more effective catalysts for $A_{Ac}2$ hydrolyses of carboxylic esters, but that the opposite would be true for $A_{Ac}1$ and $A_{Al}1$ hydrolyses in which a carbonium ion is formed in the slow step.

The acid hydrolyses examined in this work were (i) hydrolyses of ethyl acetate and methyl benzoate (mechanism $A_{Ac}2$), (ii) hydrolysis of methyl mesitoate (mechanism $A_{Ac}1$), and (iii) hydrolysis of *t*-butyl acetate (mechanism $A_{Al}1$). One major difference between an A1 and A2 ester hydrolysis is that in the latter, the transition state contains at least one water molecule and should have a number of acidic protons which can hydrogen bond strongly to water,[12] *e.g.*



For none of these reactions is there reason to expect any extra catalytic effectiveness of the halogen acids

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[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapters VII and XIV.

[3] F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

[4] J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956 (1961), accompanying papers, and references cited therein.

[5] C. A. Lane, *ibid.*, **86**, 2521 (1964).

[6] K. Yates and R. A. McClelland, *ibid.*, **89**, 2686 (1967).

[7] J. F. Bunnett and F. R. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1967).

[8] (a) F. A. Long, W. F. McDevit, and F. B. Dunckle, *J. Phys. Colloid Chem.*, **55**, 813 (1951); (b) D. McIntyre and F. A. Long, *J. Amer. Chem. Soc.*, **76**, 3240 (1954).

[9] C. A. Bunton and J. H. Fendler, *J. Org. Chem.*, **30**, 1365 (1965); **31**, 3764 (1966).

[10] C. A. Bunton, N. A. Fuller, S. G. Perry, and J. Pitman, *J. Chem. Soc.*, 4478 (1962).

[11] C. T. Chmiel and F. A. Long, *J. Amer. Chem. Soc.*, **78**, 3326 (1956).

[12] This argument does not depend upon the structure of the conjugate acid and is not materially affected by the particular structure assumed for the transition state of the $A_{Ac}2$ hydrolysis.

due to nucleophilic attack by the halide ion upon the conjugate acid.[13]

If these differences stem from the differing extents of hydrogen bonding between the transition states and water they should also appear in equilibria, and Arnett and Mach have shown that the relation between the H_0', H_0''', and H_R scales depends upon the nature of the strong acid.[14] In strong acids we cannot generally determine the activity coefficients of the indicator bases, and part of the specificity of the acids could arise here. Therefore we examined the salt effects upon the ionization of *p*-nitroaniline and tri-*p*-anisylmethanol in dilute acid, so that we could eliminate the effects of salts upon the activity coefficients of the bases.

Salt effects upon H_0' have been shown to be less than upon H_R[15,16] but the range of salts was not large enough to show differences in their behavior, and the electrolyte effects upon the activity coefficients of the indicator alcohol were not determined.

Experimental Section

Materials. *p*-Nitroaniline (Aldrich) was recrystallized twice from aqueous alcohol, mp 148° (lit.[17] mp 147–148°); tri-*p*-anisylmethanol was prepared by the oxidation of the triarylmethane with lead dioxide[18] and purified by chromatography over alumina, mp 84° (lit.[18] mp 83.5–84°). It was converted into the red perchlorate salt by dissolving it in warm 72% perchloric acid and diluting the solution with water.

Ethyl acetate (Baker and Adamson Reagent Grade) was purified by distillation, taking the fraction boiling at 76–76.5°, and methyl benzoate (Eastman Reagent Grade) was vacuum distilled, taking the fraction boiling at 75° (16 mm).

t-Butyl benzoate was prepared from the alcohol and benzoyl chloride in pyridine[19] and purified by vacuum distillation, bp 65° (1 mm) (lit.[20] bp 67–68° (1 mm)).

Methyl mesitoate was prepared from methanol and mesitoyl chloride in pyridine,[21] bp 103–103.5° (3 mm) (lit.[21] bp 77–79° (1 mm), 114.8–115.2° (7 mm)).

The acids were commercial samples and the salts were dried before use in a vacuum oven or were prepared *in situ* by neutralization of acid by alkali.

Indicator Measurements. The indicator ratios were measured spectrophotometrically at 25° using a PE-Hitachi 139 or a Gilford 220 spectrophotometer, following procedures already described.[22,23]

The absorbances at 4820 Å were measured for tri-*p*-anisylmethanol in 0.15 *M* perchloric acid plus the added salts and compared with the absorbance in 3 *M* perchloric acid, where the alcohol is converted wholly into the carbonium ion.[23] We were unable to obtain consistent values for the solubility of tri-*p*-anisylmethanol in sodium *p*-toluenesulfonate. Therefore we used sodium methanesulfonate, made measurements on both indicator systems using it, and then obtained consistent results.

We used 0.1 *M* HCl as our standard for H_0', following Paul and Long,[22] but we used 0.15 *M* $HClO_4$ for H_R, so that we could work in a convenient range of indicator ratios. However these salt effects are independent of small changes in acid concentration.[22]

The values of H_0' for hydrochloric, hydrobromic, and sulfuric acids are taken from the compilation of Paul and Long, and for perchloric acid we used the more recent values of Yates and Wai.[22] (The various sets of H_0' agree within experimental error for the acid concentrations used in this work.)

Activity Coefficients. The activity coefficients of methyl benzoate and mesitoate were determined by distribution between carbon tetrachloride and the aqueous solution.[24] The concentration of the ester in the aqueous layer was determined spectrophotometrically from the absorbances at 2300 Å for methyl benzoate and 2400 Å for methyl mesitoate after centrifugation of the solution.

The activity coefficients of *p*-nitroaniline in neutral aqueous salt solutions were taken from the data of Paul[25] or were determined at 25°, following his procedure with 0.5 and 1.0 *M* salts.

The activity coefficients of tri-*p*-anisylmethanol in 0.5 and 1.0 *M* neutral aqueous salt solutions were determined by solubility measurements at 25°. Perchloric acid (3 *M*) was added to the saturated solution after filtration to convert the carbinol completely into the carbonium ion and the absorbance was measured at 4820 Å.

Kinetics. The reactions were generally followed by spectrophotometrically using a Gilford 220 spectrophotometer with thermostated cell compartments. The hydrolysis of ethyl and *t*-butyl acetates at 25° was followed in stoppered cells by measuring the absorbance at 2110 Å, except for hydrolysis in hydrobromic acid which was of necessity followed dilatometrically. Where comparisons were made our rate constants agreed well with those of Bell, Dowding, and Noble.[26]

The hydrolysis of methyl benzoate was followed by a method similar to that of Chmiel and Long.[11] Portions of the reaction mixture were added to sufficient borate buffer to neutralize the mineral acid and convert benzoic acid into benzoate ion. The absorbance was then measured at 2300 Å. This method was also used for following the hydrolysis of *t*-butyl benzoate, except that because of the unreactivity of this ester toward hydroxide ion we used sodium hydroxide to neutralize the acid.

The method of Chmiel and Long was used to follow the hydrolysis of methyl mesitoate.[11] Portions (5 ml) of the reaction mixture were neutralized with sodium hydroxide and extracted with methylene chloride. The aqueous layer was then acidified and its absorbance measured at 2350 Å. Because of the decarboxylation of mesitoic acid the absorbance corresponding to complete reaction was calculated from the initial concentration of methyl mesitoate determined spectrophotometrically using ϵ 3770 at 2400 Å; for mesitoic acid we found ϵ 2720 at 2350 Å.

For the hydrolysis of methyl mesitoate we were able to follow only the first 60–70% of reaction, because of the decarboxylation of mesitoic acid. Our rate constants agreed reasonably well with those of Chmiel and Long,[11] where comparisons can be made, although for methyl benzoate our rates for perchloric acid are slightly higher than theirs. There were problems in following the hydrolysis of *t*-butyl benzoate because bubbles, probably of isobutylene, formed during reaction. This problem was most serious in sulfuric acid, where we could not use high acid concentrations. The rate constants for the hydrolyses of methyl mesitoate and *t*-butyl benzoate are less accurate than the others.

Kinetic salt effects were only examined for the hydrolyses of the acetates which were followed spectrophotometrically. We could only use salts whose solutions were transparent at 2110 Å and were therefore restricted to chlorides and perchlorates. We did not use bisulfates because of the problem of the second dissociation of sulfuric acid.

First-order rate constants, k_ψ (sec^{-1}), were calculated graphically using the integrated first-order rate equation or Guggenheim's modification of it.[27]

Results

Kinetics. Acid Hydrolyses. The rate constants for the A2 hydrolyses of ethyl acetate and methyl ben-

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zoate are given in Tables I and II together with some of the results of Bell, Dowding, and Noble for the hydrochloric and sulfuric acid catalyzed hydrolysis of ethyl acetate,[26] and those of Chmiel and Long for the hydrolyses of methyl benzoate in perchloric acid.[11]

Table I. Acid Hydrolysis of Ethyl Acetate^a

Acid	C_{H^+}, M	10^4k_ψ, sec^{-1}
$HClO_4$	0.15	0.17
$HClO_4$	2.17	2.51
$HClO_4$	3.16	3.82
$HClO_4$	4.09	4.32
$HClO_4$	5.50	5.54
$HClO_4$	7.23	6.51
HCl	0.457	0.52^b
HCl	2.11	2.74^b
HCl	3.09	4.50^b
HCl	3.55	5.56
HCl	4.00	6.45^c
HCl	5.48	10.4^b
HCl	7.91	20.2^b
HBr	2.62	3.60^c
HBr	3.34	4.73^c
HBr	3.96	6.10^c
HBr	4.97	8.23^c
HBr	5.72	9.19^c
H_2SO_4	2.85	5.61^b
H_2SO_4	3.08	6.55^b
H_2SO_4	4.25	10.4^b
H_2SO_4	6.75	19.2^b

[a] At 25.0° in aqueous acid. [b] See ref 26; reaction followed dilatometrically. [c] This work, reaction followed dilatometrically.

Table II. Acid Hydrolyses of Methyl Benzoate^a

Acid	C_{H^+}, M	10^5k_ψ, sec^{-1}
HCl	1.19	31.5
HCl	1.81	47.8
HCl	2.40	67.0
HCl	3.44	115
HCl	4.04	136
$HClO_4$	0.98	18.7^b
$HClO_4$	1.69	37.5
$HClO_4$	1.93	36.6^b
$HClO_4$	2.44	52.5
$HClO_4$	3.82	74.5^b
$HClO_4$	3.89	81.9
$HClO_4$	4.54	99.6
H_2SO_4	1.17	34.5
H_2SO_4	1.76	49.7
H_2SO_4	2.59	88.1
H_2SO_4	3.29	130

[a] At 90.0° in aqueous acid. [b] See ref 11.

The values of k_ψ for the $A_{Ac}1$ hydrolysis of methyl mesitoate are given in Table III and those for the $A_{Al}1$ hydrolyses of *t*-butyl acetate and benzoate are in Tables IV and V. Our values of k_ψ for the hydrolysis of *t*-butyl acetate in hydrochloric acid are slightly larger than those of Salomaa,[28] possibly because we followed the reaction spectrophotometrically using very low ester concentrations, whereas Salomaa used a titrimetric method and high ester concentrations.

These ester hydrolyses do not precisely fit either of the limiting kinetic forms predicted by the Zucker–Hammett hypothesis.[3]

Table III. Acid Hydrolysis of Methyl Mesitoate^a

Acid	C_{H^+}, M	10^5k_ψ, sec^{-1}
HCl	3.56	0.55
HCl	4.42	1.41
HCl	5.42	4.31
HCl	6.05	9.16
$HClO_4$	1.00	0.073^b
$HClO_4$	1.93	0.42^b
$HClO_4$	2.56	0.94
$HClO_4$	2.75	0.92
$HClO_4$	2.88	0.97
$HClO_4$	2.94	1.16^b
$HClO_4$	2.96	1.80^b
$HClO_4$	3.79	4.30
$HClO_4$	3.90	5.60^b
$HClO_4$	4.39	12.7^b
$HClO_4$	4.80	26.0^b
$HClO_4$	5.36	67.0^b
$HClO_4$	5.76	114^b
H_2SO_4	3.12	1.0^b
H_2SO_4	4.16	3.1^b
H_2SO_4	5.00	15.5^b
H_2SO_4	6.14	42^b

[a] At 90.0° in aqueous acid. [b] See ref 11.

Table IV. Acid Hydrolysis of *t*-Butyl Acetate^a

Acid	C_{H^+}, M	10^4k_ψ, sec^{-1}	Acid	C_{H^+}, M	10^4k_ψ, sec^{-1}
$HClO_4$	0.15	0.22	HCl	1.58	4.78
$HClO_4$	0.89	2.23	HCl	2.01	9.15
$HClO_4$	1.20	4.46	HCl	2.12	11.3
$HClO_4$	1.37	5.51	HCl	2.56	19.4
$HClO_4$	1.45	6.95	HCl	2.65	20.3
$HClO_4$	1.68	9.45	HCl	2.96	27.8
$HClO_4$	1.78	11.8	HCl	2.97	28.8
$HClO_4$	1.84	13.4	HCl	3.63	68.3
$HClO_4$	1.94	14.0	HCl	3.87	85.1
$HClO_4$	1.99	17.3	H_2SO_4	1.32	4.63
$HClO_4$	2.10	17.7	H_2SO_4	1.48	6.25
$HClO_4$	2.40	28.3	H_2SO_4	1.57	7.01
$HClO_4$	2.52	36.6	H_2SO_4	1.98	13.1
$HClO_4$	2.66	50.1	H_2SO_4	2.22	20.9
$HClO_4$	2.80	60.5	H_2SO_4	2.53	32.9
$HClO_4$	2.97	72.7	H_2SO_4	2.70	41.6
$HClO_4$	2.98	75.2	H_2SO_4	3.47	132
$HClO_4$	3.23	141			
$HClO_4$	3.55	227			

[a] At 25.0° in aqueous acid.

Table V. Acid Hydrolysis of *t*-Butyl Benzoate^a

Acid	C_{H^+}, M	$10^4k_\psi/h_0$	Acid	C_{H^+}, M	$10^4k_\psi/h_0$
$HClO_4$	1.05	1.81	HCl	1.37	1.73
$HClO_4$	1.28	2.96	HCl	2.51	5.47
$HClO_4$	1.60	4.21	HCl	3.00	7.25
$HClO_4$	1.62	4.60	HCl	3.00	8.86
$HClO_4$	2.04	5.25	HCl	3.16	8.00
$HClO_4$	2.22	7.02	HCl	3.21	9.27
$HClO_4$	2.28	7.77	HCl	3.78	11.9
$HClO_4$	2.28	8.17	HCl	3.82	16.3
$HClO_4$	2.48	11.2	HCl	4.01	17.2
$HClO_4$	2.53	11.2	HCl	4.01	18.2
$HClO_4$	2.57	10.2	HCl	4.53	32.9
$HClO_4$	2.73	15.7	HCl	4.53	28.7
$HClO_4$	2.86	16.2			
$HClO_4$	3.09	18.2			
$HClO_4$	3.17	21.5			
H_2SO_4	1.13	1.15			
H_2SO_4	1.90	2.72			
H_2SO_4	2.03	5.55			
H_2SO_4	2.25	6.81			

[a] At 25.0° in aqueous acid.

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(28) P. Salomaa, *Suomen Kemistilehti*, **B32**, 145 (1959).

The variation of rates with acidity fit the linear free energy relation of Bunnett and Olsen reasonably well and plots of log $k_\psi + H_0$ against $-(H_0 + \log C_{H^+})$ are generally linear, as had been noted earlier for the ester hydrolyses for which data were available.[7] However, we are concerned with the catalytic efficiencies of the different acids in the presence or absence of electrolytes rather than with the form of the variation of rate with stoichiometric acidity or protonating power, and we therefore merely compare the values of k_ψ at particular values of C_{H^+} or H_0'.

Kinetic Salt Effects. Many added salts increase the protonating power of the medium, as measured by Hammett's acidity function,[22,25,29] and therefore generally assist acid hydrolyses. Added chlorides and perchlorates assist the hydrolyses of ethyl and *t*-butyl acetate in aqueous 0.15 *M* perchloric acid (Table VI), but the $A_{Ac}2$ hydrolysis of ethyl acetate is assisted more by chlorides than by perchlorates, although the opposite is true for the $A_{Al}1$ hydrolysis of *t*-butyl acetate, as can be seen from the values of $(\log \Delta k_\psi)/c_s$ in Table VI (Δk_ψ is the increase of k_ψ brought about by added salt). The salt effects are approximately independent of temperature.

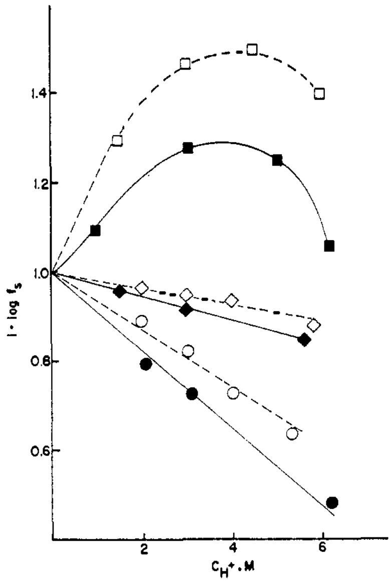

Figure 1. Activity coefficients of methyl benzoate and mesitoate in aqueous acids at 25°: methyl benzoate (solid lines), ●, $HClO_4$; ■, H_2SO_4; ◆, HCl; methyl mesitoate (broken lines): ○, $HClO_4$; □, H_2SO_4; ◇, HCl.

Table VI. Kinetic Salt Effects on the Hydrolysis of Ethyl and *t*-Butyl Acetates[a]

Substrate	Salt	C_{salt}, *M*	$10^4 k_\psi$, sec^{-1}	Log $\Delta k_\psi / c_s$
Ethyl acetate	...	...	0.17	...
Ethyl acetate	...	...	0.40[b]	...
Ethyl acetate	LiCl	2.0	0.23	0.06
Ethyl acetate	LiCl	2.0	0.68[b]	0.12[b]
Ethyl acetate	LiCl	4.0	0.36	0.08
Ethyl acetate	LiCl	4.0	1.12[b]	0.11[b]
Ethyl acetate	NaCl	2.0	0.23	0.06
Ethyl acetate	NaCl	2.0	0.67[b]	0.11[b]
Ethyl acetate	NaCl	4.0	0.36	0.08
Ethyl acetate	NaCl	4.0	0.98[b]	0.10[b]
Ethyl acetate	$LiClO_4$	2.0	0.17	0.00
Ethyl acetate	$LiClO_4$	2.0	0.41[b]	0.00[b]
Ethyl acetate	$LiClO_4$	4.0	0.18	0.00
Ethyl acetate	$LiClO_4$	4.0	0.42[b]	0.00[b]
Ethyl acetate	$NaClO_4$	2.0	0.17	0.00
Ethyl acetate	$NaClO_4$	2.0	0.45[b]	0.03[b]
Ethyl acetate	$NaClO_4$	4.0	0.17	0.00
Ethyl acetate	$NaClO_4$	4.0	0.47[b]	0.02[b]
t-Butyl acetate	...	...	0.22	...
t-Butyl acetate	...	...	1.03[b]	...
t-Butyl acetate	LiCl	2.0	1.00	0.32
t-Butyl acetate	LiCl	2.0	3.69[b]	0.28[b]
t-Butyl acetate	LiCl	3.0	2.43	0.35
t-Butyl acetate	NaCl	2.0	0.83	0.29
t-Butyl acetate	NaCl	2.0	4.23[b]	0.31[b]
t-Butyl acetate	NaCl	3.0	1.38	0.27
t-Butyl acetate	$LiClO_4$	2.0	1.73	0.45
t-Butyl acetate	$LiClO_4$	2.0	5.45[b]	0.35[b]
t-Butyl acetate	$LiClO_4$	3.0	4.50	0.44
t-Butyl acetate	$NaClO_4$	2.0	1.21	0.37
t-Butyl acetate	$NaClO_4$	2.0	4.63[b]	0.33[b]
t-Butyl acetate	$NaClO_4$	3.0	2.67	0.39

[a] In aqueous 0.15 *M* $HClO_4$ at 25.0°. [b] At 35.0°.

Activity Coefficients. The relation between the molar activity coefficients, f_s, for methyl benzoate and mesitoate and acid concentration is shown in Figure 1. The acid hydrolysis of *t*-butyl benzoate is too fast for us to be able to measure its activity coefficient under these conditions. The variation of the activity coefficients of these methyl esters with the nature and concentration of the acids follows the same general pattern found for carboxylic anhydrides and other polar nonelectrolytes,[9,24] and acids "salt out" methyl mesitoate relative to their effect on methyl benzoate. The Setschenow parameters, K_s, for *p*-nitroaniline and trianisylmethanol are given in Table VII and follow the expected pattern.[24]

Table VII. Salt Effects upon H_0' and H_R[a]

Salt	$\Delta H_0'$	$-\Delta H_R$	Δ log a_{H_2O}[c]	$-\Delta$ log f_{ROH}	Δ log f_B	Δ log f_{HB^+}/f_{R^+}
LiCl	−0.23	0.35	−0.02	−0.27	0.08	−0.09
NaCl	−0.20	0.35	−0.01	−0.21	0.07	0.00
$NaNO_3$	−0.20	0.47	−0.01	−0.20	−0.02	0.04
NaBr	−0.21	0.42	−0.02	0.05	0.04	0.28
$NaCH_3SO_3$	−0.05	0.29	−0.01[d]	0.12	0.05	0.40
$LiClO_4$	−0.30	0.82	−0.02	0.17	−0.07	0.58
$NaClO_4$	−0.25	0.86	−0.01	0.07	−0.08	0.59
$NaC_7H_7SO_3$	0.06[b]	0.6	−0.01	...	−0.51[b]	...

[a] For 1 *M* salt at 25.0°. [b] See ref 3. [c] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co., Ltd., London, 1965, Appendix 8. [d] Assumed to be the same as for sodium tosylate.

Acidity Functions. The salt effects of anions upon the H_0' and H_R functions are different (Figures 2 and 3); in particular perchlorates increase $-H_R$ much more than $-H_0'$.

The changes in the acidity functions are given by

$$\Delta H_0' = (H_0')_{0.1\,M\,\mathrm{HCl + salt}} - (H_0')_{0.1\,M\,\mathrm{HCl}} \equiv$$

$$-\log\left(\frac{C_{BH^+}}{C_B}\right)_{0.1\,M\,\mathrm{HCl + salt}} + \log\left(\frac{C_{BH^+}}{C_B}\right)_{0.1\,M\,\mathrm{HCl}}$$

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(29) G. Harbottle, *J. Amer. Chem. Soc.*, 73, 4024 (1951).

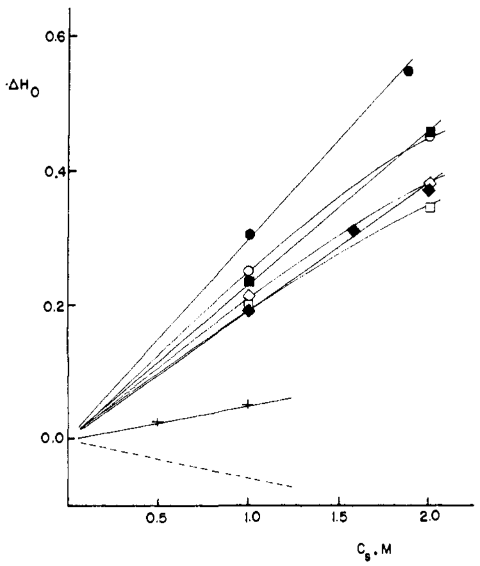

Figure 2. Salt effects upon $\Delta H_0'$ in 0.1 M hydrochloric acid: ●, $LiClO_4$; ○, $NaClO_4$; ■, LiCl; □, NaCl; ◆, $NaNO_3$; ◇, NaBr; +, NaOMes; broken line is for sodium tosylate.[3]

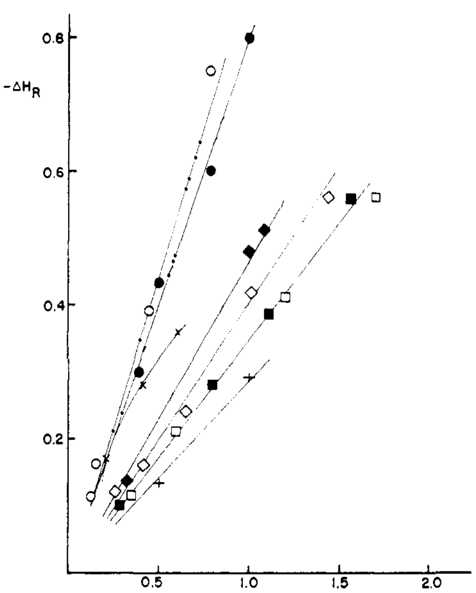

Figure 3. Salt effects upon ΔH_R in 0.15 M perchloric acid: ●, $LiClO_4$; ○, $NaClO_4$; ■, LiCl; □, NaCl; ◆, $NaNO_3$; ◇, NaBr; +, NaOMes; ×, NaOTos.

and

$$\Delta H_R = (H_R)_{0.15\,M\ \mathrm{HClO_4+salt}} - (H_R)_{0.15\,M\ \mathrm{HClO_4}} \equiv -\log\left(\frac{C_{R^+}}{C_{ROH}}\right)_{0.15\,M\ \mathrm{HClO_4+salt}} + \log\left(\frac{C_{R^+}}{C_{ROH}}\right)_{0.15\,M\ \mathrm{HClO_4}}$$

They vary approximately linearly with salt concentration. Our values for $\Delta H_0'$ agree well with those of Paul and Long,[22] except for sodium perchlorate, where we find a slightly larger effect. However even here the discrepancy is not much greater than the uncertainty of 0.05 unit which Paul and Long quote as the reliability of measurements of acidity functions. (In Figure 2 the value of $\Delta H_0'$ for 1 M sodium perchlorate is the mean of two values, agreeing within 0.01, and that for 1 M lithium perchlorate is the mean of three, also agreeing within 0.01 unit.)

Discussion

Acidity Function. We will first consider salt effects upon acid-base equilibria, because no question of reaction mechanism is then involved. We cannot determine the effects of added electrolytes upon the activity coefficients of the individual cations, but only the relative effects upon the carbonium ion and the *p*-nitroanilinium ion.

For the salt effects upon the ionizations of a Hammett base B and an alcohol ROH

$$B + H^+ \rightleftharpoons HB^+$$
$$ROH + H^+ \rightleftharpoons R^+ + H_2O$$

we can write

$$\Delta \log\left(\frac{f_{HB^+}}{f_{R^+}}\right) = \Delta H_0 - \Delta H_R + \Delta \log\left(\frac{f_B}{f_{ROH}}\right) + \Delta \log a_{H_2O}$$

where each of the terms relates to the change in the property brought about by addition of the salt, and that for the activity coefficients of the indicators is given by the Setschenow parameters.

The values of the various terms, and of $\Delta \log (f_{HB^+}/f_{R^+})$, are given in Table VII for 1 M salts. There is considerable uncertainty in some of the terms in this table, and the differences between $\Delta \log (f_{HB^+}/f_{R^+})$ for some of the salts are within experimental error, but nonetheless there is a clear trend in the ratio of the ionic activity coefficients as we go down the table. The differential specific salt effects upon the H_0' and H_R functions depend largely upon changes in the ratio of the activity coefficients of carbonium and anilinium ions.

For the ionization of the alcohol only one water molecule is included formally in the equilibrium. Hydration of the various species involved in both equilibria must be important,[4,7,30] but we cannot account for the salt effects upon $\Delta \log (f_{HB^+}/f_{R^+})$ simply by putting the activity of water raised to some power into the equilibrium equation.

We have restricted our study to uni-univalent salts because of problems of ionic equilibria in acid, but the predominant effects seem to be caused by the anion, and the order of effectiveness of the anions in stabilizing the carbonium ion, relative to their effect upon the anilinium ion, is $ClO_4^- > CH_3SO_3^- > Br^- > NO_3^- > Cl^-$.

Paul and Long noted a relation between the salt effect upon the activity coefficient of *p*-nitroaniline and upon H_0' in 0.1 M hydrochloric acid,[22] at least for relatively low salt concentrations (<2 M), where the activity of water is close to unity,[31] but at high salt (and acid) concentrations the changes in H_0' have been correlated reasonably well with changes in the activity of water.[15,32] These investigations indicate that salts af-

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(30) R. W. Taft, *J. Amer. Chem. Soc.*, **82**, 2965 (1960).

(31) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Butterworth and Co., Ltd., London, 1959, Appendix 8.

(32) K. N. Bascombe and R. P. Bell, *Discussions Faraday Soc.*, **24**, 158 (1957); P. A. T. Wyatt, *ibid.*, **24**, 162 (1957); D. Rosenthal and J. S. Dwyer, *Can. J. Chem.*, **41**, 80 (1963).

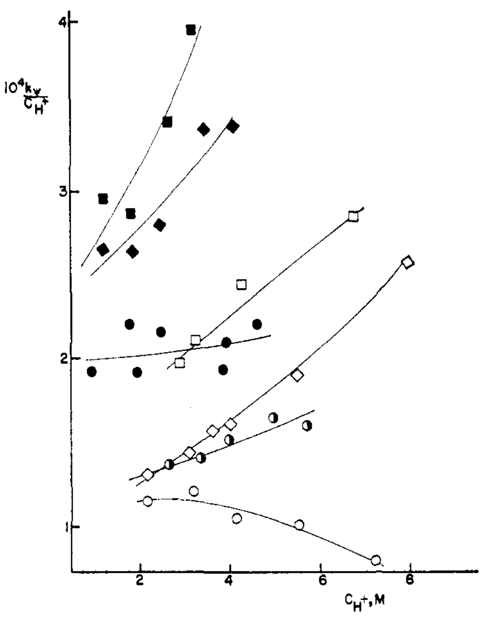


Figure 4. Effect of acids upon the second-order rate constants k_ψ/C_{H^+} for the hydrolyses of methyl benzoate and ethyl acetate: methyl benzoate; ●, $HClO_4$; ■, H_2SO_4; ◆, HCl; ethyl acetate; ○, $HClO_4$; □, H_2SO_4; ◇, HCl; ◑, HBr.

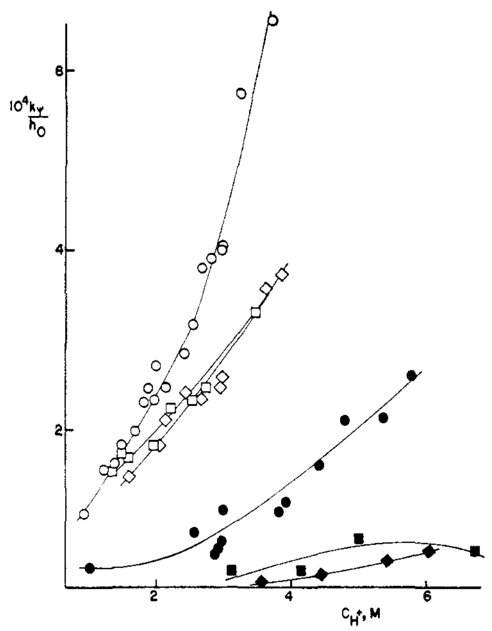


Figure 5. Effects of acids upon the second-order rate constants k_ψ/h_0 for the hydrolyses of methyl mesitoate and *t*-butyl acetate; methyl mesitoate: ●, $HClO_4$; ■, H_2SO_4; ◆, HCl; *t*-butyl acetate: ○, $HClO_4$; □, H_2SO_4; ◇, HCl.

fect the protonation of nitroanilines by changing the activity coefficient of the free nitroaniline and that of the proton and the anilinium ion by virtue of changes in the water activity.[15,32] Therefore, it appears that electrolytes do not have large specific effects upon the free energies of the anilinium ions and that their effect upon them is largely indirect and exerted through changes in the water activity, as suggested by Taft's explanation of the differential protonation of primary, secondary, and tertiary amines in terms of the differing numbers of ammonium hydrogen atoms which can be solvated by water.[30]

If we assume that the activity coefficient, f_{HB^+}, of *p*-nitroaniline is not affected specifically by the various salts, other than indirectly by a small effect upon water activity, we must also assume that there is a specific salt effect upon the activity coefficient of the carbonium ion and that perchlorate, methanesulfonate, and bromide ions stabilize the carbonium ion much more than do chloride or nitrate ions.

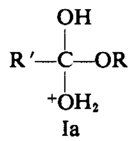
In the carbonium ion the positive charge is delocalized over the anisyl groups, whereas in the anilinium ion it is concentrated on the relatively small ammonium residue, and it seems that a large anion of low charge density like perchlorate is efficient at stabilizing a large cation also of low charge density, such as the tri-*p*-anisylmethyl cation. Our experiments on these salt effects therefore agree with the demonstration by Arnett and Mach that the differences between H_0' and H_R, for a given molarity of acid, increase in the sequence $HCl < H_3PO_4 < H_2SO_4 < HClO_4$.[14]

Effects of Acids and Reaction Mechanism. The systematic differences in the catalytic powers of the strong acids depend upon reaction mechanism rather than ester structure. The variations of the activity coefficients with acidity are similar for methyl benzoate and mesitoate (Figure 1), as is probably also true for the other esters, and activity coefficients for both methyl benzoate and mesitoate decrease in the sequence $H_2SO_4 > HCl > HClO_4$. If only initial-state effects were important this sequence should apply also to reaction rates, as is found for $A_{Ac}2$ hydrolyses of carboxylic esters and anhydrides (Tables I and II and ref 9), but for the A1 hydrolyses the acid sequence upon the rates is opposite to that expected in terms of the initial-state effects (Tables III–V) and the differential kinetic effects of the strong acids must therefore depend to some extent upon the reaction mechanism.

There is a real problem in comparing the catalytic effectiveness of the acids, *e.g.*, the rate comparisons would be made in terms of either hydrogen ion concentration or protonating power as measured by, say, Hammett's or any other acidity function. However the acid order for a given reaction mechanism does not appear to depend upon the choice of the acidity scale. The values of the second-order rate constants, k_ψ/C_{H^+} and k_ψ/h_0, are given either in Table V or Figures 4 and 5, and in all the cases we find for the A1 reactions that they are in the sequence $HClO_4 > HCl \sim H_2SO_4$, but for the A2 reactions it is $H_2SO_4 > HCl \sim HBr > HClO_4$. The values of k_ψ/C_{H^+} and especially of k_ψ/h_0 for methyl mesitoates and *t*-butyl benzoate are scattered (Experimental Section) whether we consider our values or those of Chmiel and Long,[11] and we chose a sensitive measure simply to illustrate the differences between the second-order rate constants for the acids. Depending upon the catalyzing acid the results sometimes quite fortuitously fit the predictions of the Zucker–Hammett hypothesis.[3]

The effectiveness of perchloric acid as a catalyst for A1 ester hydrolyses and its ineffectiveness for A2 hydrolyses are shown very well in Figures 4 and 5. The differences between the acids become apparent at quite low concentrations, as for anhydride hydrolyses.[9]

In an $A_{Ac}2$ hydrolysis of a carboxylic ester or anhydride the transition state has a considerable amount of positive charge localized upon good hydrogen bonding centers, *i.e.*, its structure should be similar to those of the tetrahedral intermediates.



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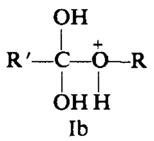
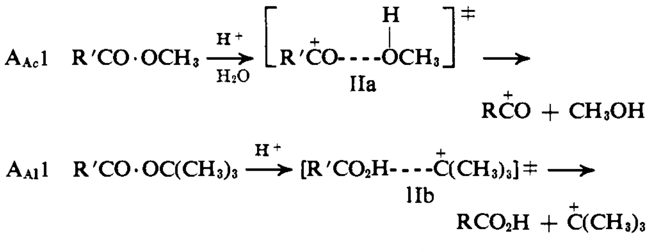


Ib

On the other hand, the transition state for the $A_{Ac}1$ and $A_{Al}1$ hydrolyses of methyl mesitoate and *t*-butyl acetate and benzoate, respectively, should have considerable carbonium ion character, as in



$$A_{Ac}1 \quad R'CO \cdot OCH_3 \xrightarrow[H_2O]{H^+} \left[R'\overset{+}{C}O \cdots \overset{H}{\underset{|}{O}}CH_3\right]^{\ddagger}_{IIa} \longrightarrow R\overset{+}{C}O + CH_3OH$$

$$A_{Al}1 \quad R'CO \cdot OC(CH_3)_3 \xrightarrow{H^+} [R'CO_2H \cdots \overset{+}{C}(CH_3)_3]^{\ddagger}_{IIb} \longrightarrow RCO_2H + \overset{+}{C}(CH_3)_3$$

The Brønsted–Bjerrum rate equations are given in eq 1 and 2 (only one water molecule is formally included in

$$\text{A1} \qquad k_\psi' = k_0'a_{H^+}f_s/f_\ddagger' \qquad (1)$$

$$\text{A2} \qquad k_\psi'' = k_0''a_{H^+}a_{H_2O}f_s/f_\ddagger'' \qquad (2)$$

the transition state in accord with Ingold's formal definition of molecularity.[2] The contributions of the water molecules which are solvating the initial and transition state are included in the activity coefficients).

In considering H_0' and H_R we can conclude that the electrolytes markedly affect the activity coefficients of the anilinium and carbonium ions, and similarly they affect the activity coefficients $f_\ddagger'$ and $f_\ddagger''$, and the effects are greater than would be expected from changes in the water activity.[31]

Sulfuric acid is a monobasic acid, but the hydrogen sulfate ion may be a strong enough acid to be dissociated even in moderately concentrated sulfuric acid. Most measurements suggest that this is not the case,[33] but some spectral evidence has been interpreted as showing that it is extensively dissociated even at high concentrations of sulfuric acid.[34] However, even if we have underestimated the hydrogen ion concentration of sulfuric acid by assuming that it acts as a monobasic acid we are left with the problem of explaining why perchloric acid is a better catalyst than it and hydrochloric acid for A1 but not A2 reactions.

The salt effects upon the acid hydrolyses of esters show a general relation between kinetic salt effects and reaction mechanism. Added chlorides and perchlorates increase the protonating power of acids very markedly,[22,25,29] but perchlorates are more effective than the chlorides at assisting these reactions which generate carbonium ions, *i.e.*, the ionization of trianisylmethanol (Figure 3) and the $A_{Al}1$ hydrolysis of *t*-butyl acetate, even though the opposite effect is observed for the protonation of nitroanilines (Figure 2 and ref 25, 29).

The small salt effects of sodium and lithium perchlorate upon the $A_{Ac}2$ hydrolysis of ethyl acetate, as compared with those of the chlorides (Table VI), can be ascribed in part to the ability of perchlorates to "salt-in" carboxylic esters,[24] but they should also "salt-in" *t*-butyl acetate, and therefore they must be much more effective than chlorides in stabilizing the transition state for the $A_{Al}1$ hydrolysis.

These specific salt effects upon the transition can be demonstrated by calculating the salt effects upon the ratio $f_\ddagger'/f_\ddagger''$ (Table VIII), using eq 1 and 2 and ignoring the salt effects upon the activity coefficients of the esters. All the salts stabilize the transition state for the hydrolysis of *t*-butyl, relative to that of ethyl acetate,[3] but perchlorates are much more effective than chlorides. Our values of $f_\ddagger'/f_\ddagger''$ probably underestimate the relative effectiveness of the perchlorates, which probably "salt-in" *t*-butyl more than ethyl acetate, because of its greater size.[24]

Table VIII. Specific Salt Effects upon the Transition States for $A_{Al}1$ and $A_{Ac}2$ Hydrolyses[a]

Salt	C_{salt}, *M*	$f_\ddagger'/f_\ddagger''$
LiCl	3.0	0.14
NaCl	3.0	0.24
$LiClO_4$	3.0	0.043
$NaClO_4$	3.0	0.075

[a] In 0.15 *M* $HClO_4$ at 25.0° as the standard state.

For A1 hydrolyses of carboxylic esters the effectiveness of the acids is always $HClO_4 > H_2SO_4 \sim HCl$, but the reverse order is found for acetal hydrolysis,[3,8b,35] which also follows an A1 mechanism,[3,36] and perchlorates have a smaller positive salt effect than chlorides and bromides.[36]

Long and his co-workers have shown that electrolytes have marked effects upon the activity coefficients of acetals and suggest that these effects may be responsible for both the varying catalytic effectiveness of the strong acids and the kinetic salt effects.[3,8b] Unfortunately in acetal hydrolysis we cannot compare electrolyte effects upon A1 and A2 mechanisms of substrates of the same general structure. There is considerable evidence that the transition states for hydrolyses of acetals and ketals have structures closer to those of the conjugate acids than the carbonium ions,[37] and the transition state, like the conjugate acid, should contain acidic hydrogens and hydrogen bond strongly with the solvent. The effects of acids upon A1 acetal and ester hydrolyses therefore become understandable.

Relations between Reaction Rates and Acidity Functions. In its original form, the Zucker–Hammett hypothesis related reaction rate for an A1 hydrolysis to Hammett's H_0' acidity function,[3] but electrolyte effects of salts and acids upon A2 reaction rates parallel those upon primary amine protonation, whereas those upon A1 reactions parallel those upon ionization of tertiary alcohols, although A1 reaction rates do not follow the H_R function. However, in our indicator experiments we are only considering relatively small differences between the effects of the various electrolytes, and moreover plots of log k_ψ *vs.* $-H_0'$ nearly always have slopes greater than unity for A1 reactions, so that the relation between rate and acidity falls in between that given by H_0' and H_R, and as we have noted the slope depends fortuitously upon the nature of the strong acid.

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(33) See ref 31, p 382; I. M. Klotz and C. F. Eckert, *J. Amer. Chem. Soc.*, **64**, 1878 (1942).

(34) J. T. Edward and I. C. Wang, *Can. J. Chem.*, **43**, 2867 (1953); T. F. Young, L. F. Maranville, and H. M. Smith in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p 35.

(35) M. M. Kreevoy and R. W. Taft, *ibid.*, **77**, 3146 (1955).

(36) F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).

(37) T. H. Fife and L. K. Jao, *J. Org. Chem.*, **30**, 1492 (1965); T. H. Fife, *J. Amer. Chem. Soc.*, **89**, 3228 (1967), and references cited therein.

We conclude that in considering relations between rate and acidity one must consider not only the molecularity of the reaction, but also the position of the positive charge in the transition state, especially insofar as it governs hydrogen bonding with the solvent. We are testing our generalizations that acid hydrolyses which involve transition states which are strongly hydrogen bonded to water will be favored by acids having anions of high charge density. It seems probable that an anion of low charge density, such as perchlorate, stabilizes carbonium ion like transition states.

Acknowledgments. We thank Dr. J. H. Fendler for assistance with the measurements of the activity coefficients.

Solvolysis of 7-Norbornyl *p*-Bromobenzenesulfonate[1]

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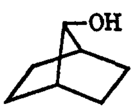
Contribution from the Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106. *Received August 25, 1967*

Abstract: Solvolysis of deuterium-labeled 7-norbornyl *p*-bromobenzenesulfonate in a variety of solvents leads to 7-norbornyl product with 10–20% inversion and 90–80% retention of configuration. From this information and literature data it is concluded that, no matter what position one takes in the nonclassical ion controversy, ionization of 7-norbornyl *p*-bromobenzenesulfonate leads to a system in which the difference in stability between classical and nonclassical ions is small.

The acetolysis of derivatives of 7-norbornanol (**1**) is an example of a solvolysis which has been interpreted in terms of both classical and nonclassical carbonium ions.[2-4] On the basis of Foote's[2] and Schleyer's[3] acetolysis rate correlations there is no evidence for anchimeric acceleration in the acetolysis of 7-norbornyl *p*-toluenesulfonate. However, product studies indicate that nonclassical ion **2** is an intermediate in the acetolysis of 7-norbornyl *p*-bromobenzenesulfonate.[4] The rearranged acetate formed in this solvolysis, 2-bicyclo[3.2.0]heptyl acetate, is exclusively the *trans* isomer. None of the *cis* isomer was detected.



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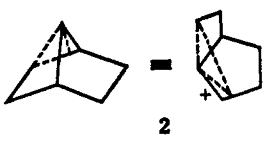

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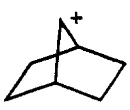

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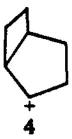

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In order to obtain further information on this apparent anomaly we have studied the solvolysis of *anti*-2,3-dideuterio-7-norbornyl *p*-bromobenzenesulfonate (**5**).[5] We find in a variety of solvents (acetic acid, aqueous methanol, aqueous acetone, and formic acid) that the 7-norbornyl product is predominantly the *anti* isomer (retention of configuration), but that 10–20% of the *syn* isomer is also formed. Results are summarized in Table I.

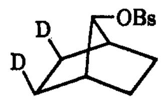
Table I. Retention of Configuration as a Function of Solvent in the Solvolysis of 2,3-Dideuterio-7-norbornyl *p*-Bromobenzenesulfonate

Solvent[a,b]	*Y*[c]	Temp, °C	Reaction time, hr	% retention
Acetic acid	−1.68	205	1.5	90 ± 5[d]
Methanol–water (70:30)	+0.96	150	20	80 ± 5
Acetone–water (50:50)	+1.40	150	20	85 ± 5
Formic acid	+2.05	100	16	85 ± 5

[a] In all cases, sufficient base was added to neutralize liberated *p*-bromobenzenesulfonic acid. Sodium acetate was used in acetic acid; sodium formate was used in formic acid; 2,6-lutidine was used in aqueous methanol and aqueous acetone. [b] Percentages given are vol % at 25°. [c] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956). [d] No change was observed in per cent retention when sodium acetate was omitted.

Deuterated *p*-bromobenzenesulfonate recovered after 90 min (*ca.* two solvolysis half-lives) in acetic acid at 205° showed 0 ± 5% ion-pair return to *syn*-deuterated *p*-bromobenzenesulfonate in the presence and in the absence of added sodium acetate.

Explanation Assuming Nonclassical Ions Are Involved. Clearly, the experimental results cannot be explained exclusively in terms of nonclassical ion **6**. Classical ion **7** is also needed. The observed predominant retention of configuration is readily explained in terms of nonclassical ion **6** (as a free ion or as an ion pair) while the 10–20% inversion observed in the 7-norbornyl product may be explained by ionization to **7** in competition with ionization to **6**, *i.e.*, by assuming



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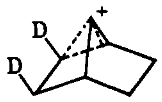

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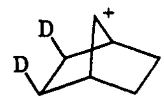

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(1) (a) A preliminary account of part of this work has appeared: F. B. Miles, *J. Amer. Chem. Soc.*, **89**, 2488 (1967). (b) P. G. Gassman and J. M. Hornback, working independently, have published a preliminary account of similar work on the corresponding *p*-toluenesulfonate: *ibid.*, **89**, 2487 (1967).

(2) C. S. Foote, *ibid.*, **86**, 1853 (1964). The fact that two of Foote's original 20 compounds have since been shown to have structures different from those accepted at the time the correlation was published does not affect the correlation appreciably. For further details, see footnote 10 of ref 1a.

(3) P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

(4) S. Winstein, F. Gadient, E. T. Stafford, and P. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(5) The terms *syn* and *anti* as used here refer to the position of the deuterium atoms with respect to the oxygen function.