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CORRELATION OF THE RATES OF REACTION OF ARENESULFONATE IONS WITH THE TRIMETHYLOXONIUM ION IN ACETONITRILE[1]

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Abstract—The kinetics of the reactions between trimethyloxonium hexafluorophosphate and a series of tetra-n-butylammonium arenesulfonates have been studied in acetonitrile at −23.4°. With the oxonium salt concentration at about 0.01 M, two series of runs were carried out; Hammett plots of the second-order rate coefficients led to ρ values of -1.18 ± 0.04 for 0.04 M arenesulfonate salt and -1.07 ± 0.02 for 0.16 M arenesulfonate salt. Solvolysis kinetics for the trimethyloxonium ion in acetonitrile are also reported.

Although trialkyloxonium (Meerwein) salts are commercially available powerful alkylating agents,[2,3] very few investigations of the kinetics or mechanism of these alkylations have been reported. Under identical conditions, the rates of hydrolysis,[4] methanolysis,[5] and solvolysis in acetonitrile[5] have been found to be greater for the trimethyloxonium ion than for the triethyloxonium ion. A detailed study of the solvent dependence of triethyloxonium ion solvolysis rates has been used to set up a scale of solvent nucleophilicities.[5] Only a minimum rate could be established for the reaction of the trimethyloxonium ion with *p*-nitrophenoxide in sulfolane[6] but, subsequently, rates were measured for reaction with thiophenoxide and *p*-nitrothiophenoxide.[7] A kinetic study of the reactivity of the trimethyloxonium ion towards benzenesulfonate ion in acetonitrile[8] was complicated by the value for the second-order rate coefficient varying with the ionic strength; such an effect is to be expected for a reaction involving two ionic species.[9]

In this investigation, we have studied reactions of the trimethyloxonium ion with a series of *para*- and *meta*-substituted arenesulfonate ions.

$$ArSO_3^- + Me_3O^+ \xrightarrow{CH_3CN} MeOSO_2Ar + Me_2O.$$

Perturbations of the second-order rate coefficients within an individual run[8,9] are minimized by using at least a 4-fold molar excess of tetra-n-butylammonium arenesulfonate over trimethyloxonium hexafluorophosphate. As one would predict for reaction between oppositely charged ions, for a given anionic reagent, the second-order rate coefficients are reduced in value as the salt concentration is increased (Table 1).

First-order rate coefficients for the background solvolysis of the trimethyloxonium ion in acetonitrile are reported in Table 2. The extrapolated value at −23.4° is 2.09×10^{-6} sec^{-1} and the rate of background solvolysis is only 1% of the rate of reaction with the lowest concentration of the slowest reacting of the added arenesulfonate anions. The enthalpy of activation, at 298.2°K, of 19.9 ± 0.2 kcal mol^{-1} is considerably less favorable than the value of 16.3 ± 0.2 kcal mol^{-1} reported[10] for acetonitrile solvolysis of methyl trifluoromethanesulfonate but this is counterbalanced by a more favorable entropy of activation of -5.5 ± 0.7 cal °K^{-1} mol^{-1} relative to -20.7 ± 0.5 cal °K^{-1} mol^{-1}.

Hammett $\rho\sigma$ plots[11] (Fig. 1) have been constructed for the two series of runs, with 0.0395 M and 0.159 M initial concentrations of tetra-n-butylammonium arenesulfonate, using average values of the data from Table 2. The slopes (Hammett ρ values) and correlation coefficients (r) are, respectively, -1.18 ± 0.04 ($r = 0.995$) and -1.07 ± 0.02 ($r = 0.996$). These values are essentially identical with the value of -1.18 ± 0.07 ($r = 0.991$) obtained, under identical conditions, for reaction of the same series of arenesulfonate anions with methyl trifluoromethanesulfonate.[10] A direct logarithmic plot of the second-order rate coefficients for the trimethyloxonium ion reaction *vs* those for the methyl trifluoromethanesulfonate reaction leads to slopes of 0.999 ± 0.032 ($r = 0.996$) and 0.897 ± 0.030 ($r = 0.993$), respectively.

Lewis and Vanderpool[6,7] have previously shown that when Hammett plots are constructed for bimolecular nucleophilic substitution reactions of methyl derivatives with anions containing a variously substituted aromatic ring, the Hammett ρ values are remarkably insensitive to the leaving-group ability of the departing anion. Their study included the trimethyloxonium ion and for this most reactive of the methyl transfer reagents, the lowest selectivity was found. However, as Lewis and Vanderpool pointed out, the reactions were approaching the diffusion controlled limit. We have used a nucleophile of considerably reduced nucleophilicity and a much lower temperature and do not have to consider any complications due to approach towards the diffusion limit. Arnett and Reich[12] have found unit slopes for the

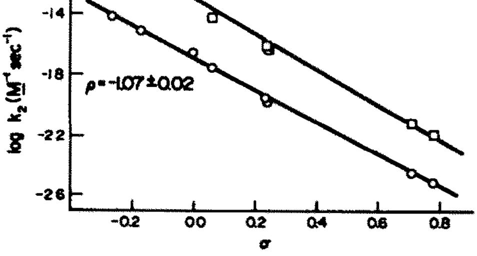

Fig. 1. Hammett plots for the reaction of Me_3OPF_6 with $ArSO_3N(n\text{-}Bu)_4$ in acetonitrile at −23.4°C. □ —— 0.04 M $ArSO_3^-$: ○ —— 0.16 M $ArSO_3^-$. Substitutents appear (from left to right) in same order as listed in Table 1.

Table 1. Second-order rate coefficients for reaction of trimethyloxonium hexafluorophosphate with 0.0395 M and 0.159 M tetra-n-butylammonium arenesulfonates (TBAA) in acetonitile at −23.4°

	0.0395 M TBAA[a]			0.159 M TBAA[a]		
Arene Subst.	$10^3[Me_3O^+]^b$	$10^3[Salt]_o^c$	$10^2k_2^d$	$10^3[Me_3O^+]^b$	$10^3[Salt]_o^c$	$10^2k_2^d$
p-OMe	8.24	41.2	10.8 ± 1.0	6.96	161.2	3.86 ± 0.49
	7.15	42.4	10.0 ± 0.5	6.89	161.1	3.72 ± 0.30
	7.07	42.4	9.6 ± 0.8	9.02	161.3	3.60 ± 0.19
	9.12	41.9	11.3 ± 0.8	8.98	160.9	3.73 ± 0.26
	9.06	42.4	9.9 ± 0.8			
p-Me	11.11	44.9	8.8 ± 0.5	10.84	162.6	3.06 ± 0.40
	11.05	44.6	8.1 ± 0.4	10.82	161.6	3.04 ± 0.39
	9.47	42.5	8.5 ± 1.0	9.31	161.7	3.14 ± 0.54
	9.51	42.6	8.2 ± 1.0	9.35	161.5	3.13 ± 0.30
None	8.93	42.1	4.9 ± 0.2	8.61	161.4	2.03 ± 0.22
	8.95	42.8	5.8 ± 0.5	8.63	161.6	1.95 ± 0.36
	8.67	43.5	5.8 ± 0.3	8.28	162.0	2.60 ± 0.22
	8.74	42.8	5.8 ± 0.4			
p-F	7.69	43.9	3.7 ± 0.2	8.36	162.8	1.67 ± 0.11
	7.81	43.5	3.5 ± 0.2	8.39	162.9	1.77 ± 0.08
p-Cl	8.82	45.0	2.40 ± 0.07	8.61	162.6	1.09 ± 0.15
	8.82	44.7	2.49 ± 0.07	8.61	162.7	1.17 ± 0.12
				8.62	164.3	1.09 ± 0.12
				8.70	164.1	1.00 ± 0.09
p-Br	8.64	44.7	2.35 ± 0.24	8.33	162.5	1.09 ± 0.11
	8.66	44.5	2.32 ± 0.12	8.25	162.6	1.02 ± 0.06
m-NO_2	8.32	45.7[e]	0.72 ± 0.04	8.24	164.7	0.36 ± 0.02
	8.31	45.6[e]	0.76 ± 0.04	8.19	164.2	0.34 ± 0.02
p-NO_2	8.55	47.0	0.63 ± 0.02	8.62	166.0	0.30 ± 0.01
	8.51	46.4	0.63 ± 0.02	8.65	165.9	0.31 ± 0.01

[a] Concentration of n-$Bu_4N^+ArSO_3^-$ at the time of mixing. [b] Concentration of $Me_3O^+PF_6^-$ at time of mixing. [c] Total salt concentration at start of run, reduced below value at mixing by reaction between Me_3O^+ and $ArSO_3^-$. [d] In units of $l\ mol^{-1}\ sec^{-1}$ and with associated standard deviations. [e] Initially 0.0388 M TBAA.

Table 2. First-order rate coefficients for solvolysis of trimethyloxonium hexafluorophosphate in acetonitrile[a,b]

Temp, °C:	−12.2	0.3	11.7	24.4
$10^4k_1(sec^{-1})$:	0.120 ± 0.006	0.698 ± 0.046	3.18 ± 0.18	15.9 ± 0.6

[a] All measurements performed, at least, in duplicate. [b] With associated standard deviations.

logarithmic plots of the second-order rate coefficients for reactions of 3- and 4-substituted pyridines in 2-nitropropane with methyl (and ethyl) iodides *vs* those for reaction with methyl fluorosulfonate, despite a difference of about 10^5 in the reactivities of the two types of alkylating agent. These studies indicate that the breakdown of the reactivity-selectivity principle found by Ritchie[13] for reactions of a series of nucleophiles with carbonium ions of a wide range of reactivity is also exhibited for, at least, some S_N2 reactions, in which the selectivity exhibited by a series of nucleophiles has been found to be almost independent of the nucleofugality of the leaving group.[14]

In the present comparison, the dimethyl ether molecule and the trifluoromethanesulfonate anion are known to have similar nucleofugalities[8] and the almost identical response of the trimethyloxonium ion and methyl trifluoromethanesulfonate to changes in the reactivity of the attacking arenesulfonate anion (as reflected by the Hammett ρ values) indicates that the selectivity exhibited towards a series of nucleophiles is independent of the charge type of the leaving group. Similarly, by competition of a series of nucleophiles against the aqueous solvent, Peterson *et al.*[15] found parallel responses to variation in nucleophilicity for methyl iodide and the cyclic tetramethyleneiodonium ion. Further, the differences observed were approximately those to be expected for consideration of a primary as opposed to a methyl substrate. The observation by Kevill and Lin[5] that a scale of solvent nucleophilicities based upon a substrate with a neutral molecule as a leaving group can be applied to bimolecular solvolyses in which the leaving group is an anion is also consistent with the conclusion from the present comparison.

EXPERIMENTAL

Materials

Trimethyloxonium hexafluorophosphate (Cationics) was found to be suitable for use as received. The purification of acetonitrile was accomplished using a previously reported procedure.[16]

The required tetra-n-butylammonium arenesulfonates were prepared from the commercially available arenesulfonyl chlorides via the Ag salt. In a typical procedure, 0.2 mol of the appropriately substituted arenesulfonyl chloride and a slight excess of silver oxide were added to 150–200 mL of distilled water (600 mL for the p-Br and p-Cl derivatives). The mixture was stirred and heated to boiling for 10 min, immediately filtered, and cooled to 0°. The crystalline ppt was vacuum dried (with protection from light) at 50° for 4–5 hr and then at 80–90° for 30 hr. The purities of the silver arenesulfonates, as determined by potentiometric titration against a standard KI soln, were at least 99.6%. The Ag salts were converted to the corresponding tetra-n-butylammonium salts by addition to an equivalent amount of tetra-n-butylammonium bromide dissolved in acetone. After warming and shaking for 20 min, AgBr was removed by filtration, the acetone was allowed to evaporate, and the resultant viscous liquid was dried under vacuum at room temp for at least 20 hr. All of the salts solidified during the drying procedure with the exception of the m-NO_2 derivative and one sample of this material did crystallize after standing for several weeks. The salts were stored in stoppered vessels within a desiccator (P_2O_5). All of the variously substituted tetra-n-butylammonium benzenesulfonates gave acceptable C, H and N analyses and the appearance and m.ps were as follows: p-OMe, colorless crystals, 100–102°; p-CH_3, colorless crystals, 69.5–71.4°; unsubstituted, colorless crystals, 74.5–75.8°; p-Cl, white waxy, 73.2–75.0°; p-Br, white waxy, 76.2–77.8°; p-F, white waxy, 68.2–70.0°; p-NO_2, pale yellow crystals, 90.0–91.5°; m-NO_2, pale yellow crystals, 38.3–39.7°.

Kinetic procedures

The solvolysis was followed by removing 5-mL portions from 50 mL of bulk soln and quenching by addition to 20 mL of a saturated neutral soln of LiCl in dry acetone, containing resorcinol blue (Lacmoid) as indicator. The unreacted trimethyloxonium ion was converted to MeCl and dimethyl ether and the nitrilium ion previously produced by solvolysis was titrated against a standardized soln of NaOMe in MeOH.[8] Infinity values were estimated by addition of a portion to 10 mL of methanol followed by titration in the usual manner after 30 min. First-order solvolysis rate coefficients (k) were calculated from the Equation

$$k = \frac{1}{t}\ln\frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

where V_0 is the titer at time zero (when first portion is removed), V_t is the titer at time (t) of removal of subsequent portion, and V_∞ is the infinity titer.

For reaction with a tetra-n-butylammonium arenesulfonate, acetonitrile and stock solns of the two reactants, maintained at −23.4°, were used to prepare 50 mL of reactant mixture. After a short period for temp reequilibration, 5 mL portions were pipetted at appropriate time intervals into 10 mL of MeOH and, after 30 min, 20 mL of acetone was added and the acid produced from unreacted oxonium ion was titrated against a standardized soln of NaOMe in MeOH, using resorcinol blue (Lacmoid) as indicator. Second-order rate coefficients were calculated from the standard form of the integrated rate equation.

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