Perchlorate Esters. Part 3.[1,2] Correlation of the Rates of Reaction of Arenesulphonate Ions with Methyl Perchlorate in Acetonitrile[3]

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Second-order rate coefficients for the reactions of acetonitrile solutions of tetra-n-butylammonium benzenesulphonate and seven *meta*- and *para*-substituted derivatives with methyl perchlorate, at 0.3°, lead to a Hammett ρ value (−1.10 ± 0.04) essentially identical to those previously reported for reactions with other powerful methylating agents. When silver ion is substituted for tetra-n-butylammonium ion, the second-order rate coefficients become concentration dependent and the fall off with increasing salt concentration can be rationalised on the basis of only free anions being reactive. The calculated degrees of dissociation are applied to the previously studied silver-ion assisted reaction of silver toluene-*p*-sulphonate with methyl iodide.

ARENESULPHONATE ions react with powerful alkylating agents to yield the alkyl arenesulphonate.[4] For methylation the mechanism is believed to be S_N2 in character.[5-7] Studies of the reactions of acetonitrile solutions of ring-substituted benzenesulphonate ions, supplied as the tetra-n-butylammonium salts, with methyl trifluoromethanesulphonate,[5] the methyl iodide–silver ion complex,[5] and the trimethyloxonium ion[7] have been extended to the somewhat less reactive[6] methyl perchlorate. For reaction with the toluene-*p*-sulphonate ion, a study has been made of the concentration dependence of the second-order rate coefficient when silver ion is substituted for the tetra-n-butylammonium ion. The results from this study are applied to data available for the reaction of silver toluene-*p*-sulphonate with methyl iodide.

EXPERIMENTAL

Acetonitrile (Mallinckrodt; Nanograde) was purified[8] and the tetra-n-butylammonium arenesulphonates prepared[7] as described previously. Silver toluene-*p*-sulphonate (Eastman) was dried overnight at 120°, immediately prior to preparation (at 0.0°) of a 0.2M solution in acetonitrile. Concentrated stock solutions of methyl perchlorate in hexane, dioxan, or benzene were prepared by the reaction of silver perchlorate with an appropriate methyl iodide solution.[9,10] Silver iodide was removed by filtration and the exact concentration of methyl perchlorate determined by addition of 1.00 ml to methanol (10 ml) and, after complete methanolysis (*ca.* 3 h), addition of acetone (20 ml) and titration against a standardized solution of NaOMe in MeOH to a Resorcinol Blue (Lacmoid) endpoint. The absence of contaminant acid was shown by addition of the stock solution (1.00 ml) to acetone (10 ml) saturated with LiCl($MeOClO_3 + LiCl \rightarrow MeCl + LiClO_4$) and titration as above; solutions used in the kinetic studies contained <1% initial acid.

Kinetic Measurements.—Stock solutions of methyl perchlorate in acetonitrile (containing 10% hexane, benzene, or dioxan) and of the appropriate arenesulphonate salt in acetonitrile were blended with the required volume of acetonitrile to make up 50.0 ml of reactant solution. After agitation and temperature requilibration, portions (5.00 ml) were pipetted, at appropriate time intervals, into methanol (10 ml) and were allowed to solvolyse at room temperature for *ca.* 3 h. After addition of acetone (20 ml), the acid developed from unchanged methyl perchlorate was titrated against a standardized solution of sodium methoxide in methanol to a Resorcinol Blue (Lacmoid) endpoint. During the time allowed for solvolysis, the extent of methanolysis of the methyl arenesulphonate product was negligible.[11] For reaction with silver toluene-*p*-sulphonate, the silver ion was precipitated prior to the titration by saturating the added acetone with LiCl. Second-order rate coefficients were calculated using the usual integrated form for the rate equation. Three illustrative runs are given in Table 1.

TABLE 1

Illustrative runs for reaction of methyl perchlorate with arenesulphonate ion in acetonitrile

(*a*) 5.00 ml portions;[a] [$MeOClO_3$] 0.006 59M; [$C_6H_5SO_3NBu^n{}_4$] 0.100M; temp. 0.3 °C; titres (ml) of 0.005 14N-NaOMe

t/min	0.0	66.6	122	191	253
Titre	6.36	5.24	4.54	3.85	3.35
10^3k_2/l mol^{-1} s^{-1}		5.19	5.17	5.17	5.18

t/min	282	529	606
Titre	3.16	2.04	1.80
10^3k_2/l mol^{-1} s^{-1}	5.16	5.04	5.04

Mean value[c] for k_2 5.14 (±0.07) × 10^{-3} l mol^{-1} s^{-1}

(*b*) 5.00 ml portions;[a] [$MeOClO_3$] 0.006 21M; [m-$NO_2C_6H_4SO_3NBu^n{}_4$] 0.0200M; temp., 0.3 °C; titres (ml) of 0.004 96N-NaOMe

t/min	0.0	243	460	1 174	1 340.
Titre	6.18	5.20	4.46	2.84	2.57
10^3k_2/l mol^{-1} s^{-1}		0.611	0.623	0.615	0.613

t/min	1 560	1 800
Titre	2.22	2.02
10^3k_2/l mol^{-1} s^{-1}	0.623	0.568

Mean value[c] for k_2 0.609 (±0.021) × 10^{-3} l mol^{-1} s^{-1}

(*c*) 5.00 ml portions;[b] [$MeOClO_3$] 0.007 60M; [p-$CH_3C_6H_4SO_3Ag$] 0.0600M; temp. 0.0 °C; titres (ml) of 0.005 62N-NaOMe

t/min	0.0	5.1	10.6	15.0	20.2
Titre	6.10	5.68	5.27	4.87	4.50
10^3k_2/l mol^{-1} s^{-1}		3.89	3.83	4.17	4.18

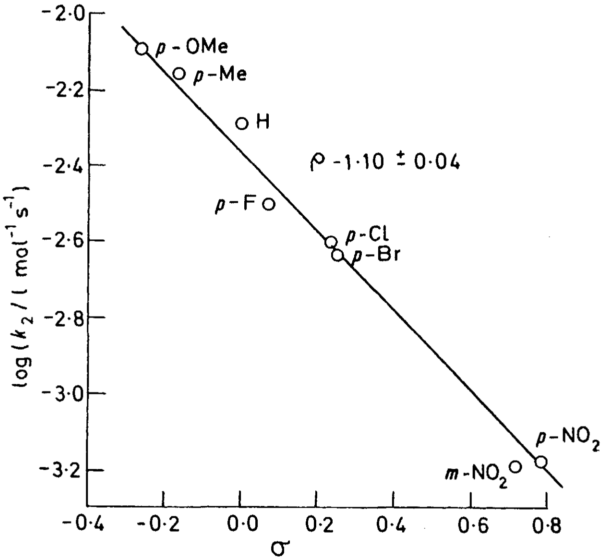
t/min	25.0	30.0	35.0	210
Titre	4.18	3.77	3.54	0.04
10^3k_2/l mol^{-1} s^{-1}	4.20	4.46	4.32	

Mean value[c] for k_2 4.15 (±0.22) × 10^{-3} l mol^{-1} s^{-1}.

[a] Solvent contains 2% (v/v) hexane. [b] Solvent contains 2% (v/v) benzene. [c] With associated standard deviation.

RESULTS AND DISCUSSION

(i) *Reaction with Tetra-n-butylammonium Arenesulphonates.*—Methyl perchlorate is solvolysed slowly[6] in acetonitrile at 0.3° and its reactions with 0.005—0.04M solutions of tetra-n-butylammonium arenesulphonate salts are sufficiently rapid that background solvolysis can



Hammett plot for the reactions of methyl perchlorate with tetra-n-butylammonium arenesulphonates in acetonitrile at 0.3 °C. The σ are taken from H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191

be neglected. In addition to an extension of the study reported [6] for the parent benzenesulphonate ion, second-order kinetics have been established for reaction of methyl perchlorate with *p*-OMe, *p*-Me, *p*-F, *p*-Cl, *p*-Br, *m*-NO_2, and *p*-NO_2 derivatives. Within the concentration range studied, the values for the second-order rate coefficient were in each case independent of the salt concentration. The values are presented in Table 2 and a Hammett plot of the data (using an average value for each substituent) is presented in the Figure. The slope of the plot (Hammett ρ value) is −1.10 ± 0.04, indicating an appreciable variation of the reaction rate as the substituent is varied. This ρ value is essentially identical to those obtained previously for displacement in acetonitrile of a variety of good leaving groups (Table 3).

TABLE 2

Second-order rate coefficients for the reaction of methyl perchlorate with tetra-n-butylammonium arenesulphonates in acetonitrile [a] at 0.3° [b]

Arene substituent	$10^3[MeOClO_3]$/M	$10^3[ArSO_3^-]$/M	10^3k_2 [c]/l mol^{-1} s^{-1}
p-OMe	6.61	5.00	7.71 ± 0.35
	3.30	10.00	8.29 ± 0.18
	6.61	10.00	8.18 ± 0.13
	6.61	20.00	7.91 ± 0.06
	6.61	40.00	8.43 ± 0.48
	3.63	10.00	8.05 ± 0.30 [d]
	6.98	10.00	7.90 ± 0.48 [e]
p-Me	7.33	5.00	7.08 ± 0.20 [e]
	8.09	10.00	6.43 ± 0.32 [e]
	4.87	10.00	6.84 ± 0.28 [d]
None	6.14	5.00	4.98 ± 0.22
	3.29	10.00	5.32 ± 0.08
	6.59	10.00	5.10 ± 0.11
	7.10	20.00	5.08 ± 0.08
	6.14	40.00	5.07 ± 0.08
p-F	8.02	5.00	3.18 ± 0.09
	8.41	10.00	3.15 ± 0.20
	8.79	20.00	2.92 ± 0.12
	8.02	40.00	3.10 ± 0.07
p-Cl	6.64	5.00	2.42 ± 0.19
	6.64	10.00	2.49 ± 0.08
	6.53	20.00	2.49 ± 0.05
	4.78	40.00	2.40 ± 0.09
p-Br	6.64	5.00	2.14 ± 0.06
	6.64	10.00	2.37 ± 0.23
	6.64	20.00	2.45 ± 0.09
	6.64	40.00	2.40 ± 0.09
m-NO_2	6.21	20.00	0.61 ± 0.03
	8.32	32.20	0.67 ± 0.04
p-NO_2	7.06	20.00	0.66 ± 0.03
	7.06	40.00	0.67 ± 0.03

[a] Except where otherwise indicated, containing 2% (v/v) hexane. [b] All runs performed, at least, in duplicate. [c] With associated standard deviations. [d] 2% Dioxan substituted for 2% hexane. [e] 4% Dioxan substituted for 2% hexane.

TABLE 3

Hammett ρ values for the reactions of acetonitrile solutions of tetra-n-butylammonium arenesulphonates with powerful methylating agents (MeX)

X	Relative reactivity [a]	Temp. (°C)	ρ [b]	r [c]	Ref.
OTf [d]		−23.6	−1.18 ± 0.07	0.991	5
OTf	17	−0.1	−1.14 ± 0.06	0.991	5
OTf		25.0	−1.06 ± 0.06	0.991	5
I-Ag^+ [e]		25.0	−0.98 ± 0.04 [f]	0.994	5
			−1.09 ± 0.05 [g]	0.992	5
$\overset{+}{O}Me_2$	190	−23.4	−1.07 ± 0.02 [f]	0.996	7
			−1.18 ± 0.04 [h]	0.995	7
$OClO_3$	1	0.3	−1.10 ± 0.04	0.989	This work

[a] Towards 0.0170M-benzenesulphonate ion in acetonitrile (from ref. 6). [b] With associated standard deviations. [c] Correlation coefficient (based, in each case, on eight data points). [d] Trifluoromethanesulphonate. [e] Silver ion substituted for tetra-n-butylammonium ion. [f] 0.16M-Arenesulphonate salt. [g] 0.005M-Silver arenesulphonate. [h] 0.04M-Tetra-n-butylammonium arenesulphonate.

A recent study [12] has shown that, even for a 10^5 difference in reactivities (methyl iodide *versus* methyl fluorosulphonate), the rates of methylation of a series of substituted pyridines show identical responses to the ring substitution. Similarly, it has been found [13] that dimethyl sulphate is consistently in the region of 4 500 times as reactive as methyl trifluoromethanesulphonate throughout reaction with a series of nucleophiles varying in strength from *m*-nitro-*NN*-dimethylaniline to thiophenoxide ion (*ca.* 10^8 range of reactivities). In view of these results, it is not surprising that constant Hammett ρ values are obtained within our study, where the relative reactivities of the methylating agents vary only over a range of *ca.* 200 from methyl perchlorate to the trimethyloxonium ion.*

(ii) *Reaction with Silver Toluene*-p-*sulphonate*.—Unlike the data for reaction with the tetra-n-butylammonium salts (Table 2), the second-order rate coefficients for reaction of methyl perchlorate with an acetonitrile solution of silver toluene-*p*-sulphonate fall in value as the salt concentration is increased (Table 4).

In the reaction of ethyl iodide with various ethoxides in ethanol, Jones *et al.*[14] have shown that the kinetics can be rationalised on the basis of free ethoxide ions being reactive and ion-pairs unreactive. For application to

* Since the silver-ion assisted reaction of methyl iodide involves rate-determining attack upon an unknown equilibrium concentration of a methyl iodide–silver ion complex, the relative reactivity for reaction of this complex cannot be determined.

TABLE 4

Comparison of the second-order rate coefficients (k_2^{exp}) for the reaction of 0.007 60M-methyl perchlorate with silver toluene-*p*-sulphonate in acetonitrile [a, b] at 0.0° with those estimated (k_2^{est}) from the value for the reaction with tetra-n-butylammonium toluene-*p*-sulphonate

[AgOTs]/M	$10^3k_2^{\mathrm{exp}}$ [c]/l mol^{-1} s^{-1}	$10^3k_2^{\mathrm{est}}$ [d]/l mol^{-1} s^{-1}
	6.84 ± 0.28 [e]	
0.005 00	6.44 ± 0.39	6.45
0.0100	6.14 ± 0.38	6.13
0.0200	5.42 ± 0.21 [f]	5.63
0.0400	5.12 ± 0.15	4.97
0.0600	4.33 ± 0.33	4.52
0.0800	4.49 ± 0.16	4.18
0.120	3.75 ± 0.15	3.71
0.160	3.69 ± 0.16	3.38

[a] Containing 2% (v/v) benzene. [b] All runs performed in duplicate. [c] With associated standard deviations. [d] $k_2^{\mathrm{est}} = \alpha k_2^{\mathrm{Bu^n{}_4NOTs}}$, where $0.077 = \alpha^2[\mathrm{AgOTs}]/(1-\alpha)$. [e] For reaction of 0.004 87M-MeOClO$_3$ with 0.0100M-Bu$^n{}_4$NOTs in acetonitrile containing 2% (v/v) dioxan (from Table 1). [f] Values of 4.95 (±0.43) × 10^{-3} and 5.35 (±0.25) × 10^{-3} l mol^{-1} s^{-1} were obtained with 0.001 90M- and 0.003 80M-MeOClO$_3$, respectively.

kinetic investigations, they suggested that the degrees of dissociation obtained from a kinetic study may be preferable to those obtained from conductivity measurements.[15]

We have not been able to find any determinations of the degree of dissociation of silver toluene-*p*-sulphonate in acetonitrile. The dissociation constant has been treated as an adjustable parameter and a value (0.077 mol l^{-1}) obtained by minimizing the deviations between experimental and calculated second-order rate coefficients for reaction with methyl perchlorate, on the basis of only free ions being reactive.[14] In conjunction with the second-order rate coefficient for reaction with the tetra-n-butylammonium salt, this value leads to very good agreement between estimated values (k_2^{est}) and experimental values (k_2^{exp}) for a silver toluene-*p*-sulphonate concentration range of 0.005—0.16M (Table 4).

The best-fit value for the dissociation constant (0.077 mol l^{-1}) is in reasonable relationship with the value of 0.015 mol l^{-1} reported[16] (at 25.0°) for silver nitrate in acetonitrile. Following the suggestion of Jones *et al.*[14] the value for the dissociation constant can be applied to the previously reported[5] study of the reaction of methyl iodide with silver toluene-*p*-sulphonate in acetonitrile. This kinetic study was at a 25° higher temperature but the effect on the dissociation constant and on the degrees of dissociation (α), calculated for a stoicheiometric concentration [AgOTs]$_s$ according to equation (1), should be modest.[17]

$$0.077 = \alpha^2[\mathrm{AgOTs}]_s/(1-\alpha) \qquad (1)$$

Pocker and Wong[18] have suggested that, in the general case, the reaction of an alkyl halide (RX) which a silver salt (stoicheiometric concentration [AgY]$_s$) can be expressed by equation (2). In equation (2), k_2° is the overall

$$\text{rate} = \alpha k_2^{\circ}[\mathrm{RX}][\mathrm{AgY}]_s + \alpha^2 k_3^{\mathrm{Y^-}}[\mathrm{RX}][\mathrm{AgY}]_s^2 \qquad (2)$$

second-order rate coefficient for unassisted and solvent-assisted reaction and $k_3^{\mathrm{Y^-}}$ is the third-order rate coefficient for anion-assisted reaction.

For reaction of methyl iodide, unassisted reaction (requiring formation of a methyl carbonium ion) seems unlikely and, for other powerful methylating agents, it has been found[5-7] that bimolecular reaction with arenesulphonate ion (>0.005M) in acetonitrile swamps out the background solvolysis. Accordingly, for reaction of silver toluene-*p*-sulphonate with methyl iodide, we would expect the first term of equation (2) to be unimportant; this view is strongly supported by the observation that the Hammett ρ value is identical to that for bimolecular attack (second-order kinetics) on either methyl perchlorate or methyl trifluoromethanesulphonate (Table 3). An analysis follows of an attempt to correlate the rates of reaction on the basis of equation (3).

$$\text{rate} = k_3^{\mathrm{exp}}[\mathrm{CH_3I}][\mathrm{AgOTs}]_s^2 = \alpha^2 k_3^{\mathrm{OTs^-}}[\mathrm{CH_3I}][\mathrm{AgOTs}]_s^2 \qquad (3)$$

The 2.5-order rate coefficients previously reported[5] have been converted to initial values for the third-order rate coefficient (k_3^{exp}) by dividing by $[\mathrm{AgOTs}]_s^{1/2}$ (Table 5). Since $k_3^{\mathrm{exp}} = \alpha^2 k_3^{\mathrm{OTs^-}}$, values of $k_3^{\mathrm{exp}}/\alpha^2$ should be constant, if the analysis is valid. It can be seen in Table 5 that, while the values are fairly constant, they pass through a minimum at around the mid-point of our concentration range. Extrapolation to either a higher or lower concentration range would lead to the value varying appreciably with concentration.

TABLE 5

Initial third-order rate coefficients [a] (k_3/l^2 mol^{-2} s^{-1}) for the reaction of silver toluene-*p*-sulphonate with methyl iodide in acetonitrile at 25.0° and attempted correction for the only partial dissociation of the silver salt [b]

[AgOTs]/M	10^3k_3	$10^3k_3/\alpha$	$10^3k_3/\alpha^2$
0.0050	10.82	11.48	12.19
0.0100	8.69	9.70	10.83
0.0200	6.46	7.84	9.52
0.0400	4.98	6.85	9.42
0.0800	3.81	6.23	10.18
0.160	3.23	6.54	13.24

[a] Calculated from the 2.5-order rate coefficients reported in ref. 5. [b] Using values for the degree of dissociation (α) estimated from reaction with methyl perchlorate at 0 °C.

While there is considerable evidence that the nucleophilicities of dissociated ions frequently (but not always[14]) are appreciably greater than when contained within an ion pair, there does not appear to have been any detailed consideration of the electrophilicity of ions [such as silver(I)] towards a halogen bonded to a saturated carbon atom. It may well be necessary to consider both free and ion-paired silver ions. In the extreme case, both types can be considered as of equal electrophilicity and, if we continue to consider only free anions as nucleophilic, the $k_3^{\mathrm{exp}}/\alpha$ values should be constant. It can be seen in Table 5 that these vary appreciably with concentration.

In particular, k_3^{exp}, $k_3^{\mathrm{exp}}/\alpha$, and $k_3^{\mathrm{exp}}/\alpha^2$ values all decrease as the concentration is increased from 0.005 to 0.04M. This suggests that intermediate analyses, in which both dissociated and undissociated ions are considered to be reactive (but with undissociated ions of reduced reactivity), will also fail to correlate the data. On reflection, it is not surprising that treatments based solely on consideration of the degree of dissociation of the silver salt fail to correlate the observed kinetics. The methyl perchlorate–silver toluene-*p*-sulphonate system (Table 4) indicates that consideration of the degree of dissociation of the salt is indeed important. However, one would expect, superimposed upon this consideration, appreciable salt concentration influences upon the second-order rate coefficient for a rate-determining step which involves interaction of an anion with a positively charged complex (Scheme 1). Support for this prediction comes from consideration of the identical charge-type reaction between trimethyloxonium hexafluorophosphate and tetra-n-butylammonium arenesulphonates (Scheme 2).[7]

$$CH_3I + Ag^+ \rightleftharpoons (CH_3IAg)^+$$

$$OTs^- + (CH_3IAg)^+ \xrightarrow{\text{r.d.s.}} CH_3OTs + AgI$$

SCHEME 1

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

SCHEME 2

Reactions of varying concentrations of a tetra-n-butylammonium arenesulphonate with a neutral ester, such as methyl trifluoromethanesulphonate [5] or methyl perchlorate (Table 2), gave constant values for the second-order rate coefficient, indicating all the anions present to be equally nucleophilic. However, for reaction with the positively charged trimethyloxonium ion, there is (as one would predict [19]) an appreciable decrease in the values for the second-order rate coefficient as the salt concentration is increased.[6,7]

One of us (M. S. B.) thanks the MARA Training Division (MRSM) (Malaysia) for a scholarship.

[0/537 *Received*, 11*th April*, 1980]

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