Perchlorate Esters. Part 9.[1] Correlation of the Rates of Solvolysis of Methyl Perchlorate using the Extended Grunwald–Winstein Equation

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The specific rates of solvolysis of methyl perchlorate in a wide variety of organic and aqueous–organic solvents have been measured and correlated by the extended Grunwald–Winstein equation. Each of the N_T and N_{OTs} scales of solvent nucleophilicity have been combined with each of the Y_{OClO_3} and Y_{OTs} scales of solvent ionizing power. The analysis shows the superiority of the Y_{OClO_3} scale for correlating perchlorate esters and indicates a sensitivity to changes in solvent nucleophilicity about equal to that found previously for the *S*-methyldibenzothiophenium ion or methyl *p*-toluenesulphonate and a sensitivity to changes in solvent ionizing power slightly less than that for methyl *p*-toluenesulphonate; these sensitivities are consistent with a conventional S_N2 mechanism for the solvolyses. A claim for nucleophilic attack by the solvent at the chlorine of a secondary perchlorate ester is discussed and an alternative, involving attack at carbon, is proposed.

Although covalent perchlorate esters have long been known,[2] it is only fairly recently that they have been extensively investigated.[3] The reluctance to study these compounds undoubtedly arises from their well-documented[4–6] unpredictable and highly explosive properties. For example, while Robertson, Annesa and Scott[7] survived a study involving the isolation and manipulation of methyl perchlorate apparently without any special precautions, an injury occurred in the work of Meyer and Spormann,[4] despite the use of special equipment and extreme caution. In our work, we have prepared perchlorate esters as fairly concentrated solutions in a saturated hydrocarbon, benzene, or dioxane by homogeneous or heterogeneous (depending on the solvent) interaction of the alkyl iodide with silver perchlorate. Further manipulations have been performed in solution, without any isolation of the ester.

We have previously reported on the kinetics and mechanism of both non-solvolytic and solvolytic reactions of methyl perchlorate. The non-solvolytic reactions involved reaction with methanol in benzene[1] or nitromethane,[8] reaction with *N,N*-dimethylanilines in benzene,[9] and reaction with arenesulphonate ions in acetonitrile.[10] Under solvolytic conditions, we have compared the rate of hydrolysis to that of ethyl perchlorate[11] and the rates of several solvolyses to those observed for other powerful methylating agents.[12] Preliminary communications of portions of this work have appeared previously.[13,14]

Other workers have investigated the reactions of methyl perchlorate with small concentrations of water, methanol or t-butyl alcohol in acetonitrile or sulpholane[15] and the reactions in various relatively powerful nucleophiles in methanol[16,17] and water.[17,18] Under solvolytic conditions, the solvolyses in dioxane–methanol,[19] acetone–methanol,[19] water–acetonitrile,[15] methanol–acetonitrile[15] and t-butyl alcohol–acetonitrile[15] mixtures have been investigated, with extension of the solvent composition range as far as the pure hydroxylic component. A very careful study of the hydrolysis in 100% water has been reported[7] and an investigation of the reactions with nucleophiles in water included a study of the background hydrolysis.[18] The solvolyses of several secondary perchlorate esters, where the perchlorate is situated at a bridging position of a cage-like hydrocarbon structure have also been investigated[20–23] and, using the specific rates of solvolysis of 2-adamtantyl perchlorate,[22,23] a Grunwald–Winstein scale of solvent ionizing power, Y_{OClO_3} values, has been developed.[24]

In the present publication, we report the values for the specific rates of solvolysis of methyl perchlorate in a wide variety of solvents. Those solvent systems for which both solvent nucleophilicity values (N_T), based upon the rates of solvolysis of the *S*-methyldibenzothiophenium ion,[25] and Y_{OClO_3} values are known have been analysed in terms of the extended Grunwald–Winstein equation, eqn. (1). In this way, one can determine both

$$\log(k/k_0) = lN + mY \qquad (1)$$

the sensitivity (l) to changes in solvent nucleophilicity values (N) and the sensitivity (m) to changes in solvent ionizing power values (Y) of the specific rates of solvolysis (k) in a series of solvents, considered relative to the specific rate of solvolysis of 80% ethanol (k_0). These sensitivity values are extremely helpful in the elucidation of the mechanism of the solvolysis reaction (1). For a model S_N1 reaction (approximated by solvolyses of

$$\mathrm{MeOClO_3 + 2SOH \longrightarrow MeOS + SOH_2^+ + ClO_4^-} \qquad (2)$$

adamantyl derivatives[24]) the l value is taken as zero and the value rises to unity (by definition) when the sensitivity towards solvent nucleophilicity parallels that of the *S*-methyldibenzothiophenium ion. Concurrent with increased sensitivity to solvent nucleophilicity, there is a decrease in the m value observed for solvolysis of an initially neutral substrate to below the value of unity (by definition) for solvolyses of the corresponding 1- or 2-adamantyl derivatives.

Results

Solvolyses in Solvents of Varying Ionizing Power.—Specific rates of solvolysis, at 24.95 °C, have been determined over the full range of composition for mixtures of the following organic solvents with water: ethanol, methanol, 2,2,2-trifluoroethanol (TFE), acetone, and dioxane. Also determined were the specific rates of solvolysis in acetic acid and isopropyl alcohol, and over the full range of composition of TFE–ethanol mixtures (Table 1). The runs were usually carried out by addition of 1 cm^3 of a stock solution of methyl perchlorate in dioxane to 49 cm^3 of the solvent or solvent mixture under investigation. In several instances, for organic solvents or for aqueous–organic mixtures with a relatively high organic component content, parallel experiments were performed in which the added stock solution was in benzene rather than dioxane.

Also contained within Table 1 are values for the specific rates estimated by use of the extended Grunwald–Winstein equation, incorporating the sensitivity values calculated from the reported data (Table 2).

Solvolyses in Methanol, Ethanol, Propan-2-ol, t-Butyl Alcohol and 80% *Ethanol*.—Specific rates of solvolysis were determined at four or five temperatures in the range 16–55 °C. Values at temperatures other than 24.95 °C (reported in Table 1) are presented in Table 3. For solvolysis in t-butyl alcohol, the integrated rate coefficients rose slightly in value with extent of reaction and initial values were obtained from a plot *vs.* extent of reaction; these initial values were used to obtain the extrapolated value at 24.95 °C (below the m.p. of the solvent) which is reported in Table 1. For each solvent, the enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation were calculated at 298 K using the specific rates at all of the temperatures studied. These activation parameters are reported in Table 3.

Effect upon the Specific Rate of Methanolysis of Added Tetra-n-butylammonium Perchlorate (*TNBAP*).—Specific rates of solvolysis were determined in solutions prepared by adding 1 cm^3 of a solution of methyl perchlorate in benzene to 49 cm^3 of methanol, at 24.95 °C, containing the desired concentration of TNBAP. The averaged specific rates determined for six concentrations of TNBAP (0.005–0.08 mol dm^{-3}) are reported in Table 4.

Discussion

Because of its explosive properties, the methyl perchlorate was prepared and used as a solution in benzene or dioxane. It was shown earlier[1] that, as prepared in benzene, no peak was observed in the ^{1}H NMR spectrum corresponding to the methyl group of toluene. In dioxane, there is the possibility of forming an oxonium ion with a reactivity similar to that of the perchlorate.[12] Strong evidence that only methyl perchlorate is formed comes from the observation that the specific rates of solvolysis are essentially identical, irrespective of whether the stock solution is in benzene or dioxane (Table 1). Further, an oxonium ion would show a very different pattern of variation of the solvolysis rates with change of solvent to that exhibited by a neutral ester, such as methyl perchlorate.[26] The slightly

Table 1. Specific rates of solvolysis (k) of methyl perchlorate,[a] at 24.95 °C, and values subsequently estimated using the extended Grunwald–Winstein equation (k_{est}).

		k/10^{-4} s^{-1}			
Code	Solvent[b]	A[c]	B[d]	k_{est}/10^{-4} s^{-1} [e]	k_{est}/10^{-4} s^{-1} [f]
1	100% EtOH	3.45 ± 0.13[g]	3.42 ± 0.12	4.3	2.8
2	90% EtOH	6.52 ± 0.09	6.37 ± 0.15	9.1	6.1
3	80% EtOH	8.45 ± 0.10[h]	8.36 ± 0.25	12.2	8.7
4	70% EtOH	9.87 ± 0.28	9.70 ± 0.18	13.5	9.9
5	60% EtOH	11.7 ± 0.3	11.2 ± 0.2	16.6	12.7
6	50% EtOH	13.7 ± 0.3	12.0 ± 0.4	15.0	11.8
7	40% EtOH	15.5 ± 0.2	—	21.6	17.6
8	30% EtOH	16.5 ± 0.5	—	26.3	22.4
9	20% EtOH	15.6 ± 0.3	—	22.5	19.7
10	100% MeOH	6.52 ± 0.18	6.80 ± 0.12[i]	7.7	5.3
11	90% MeOH	8.70 ± 0.17	8.76 ± 0.20	14.0	10.0
12	80% MeOH	11.2 ± 0.2	10.2 ± 0.1	19.1	14.0
13	70% MeOH	13.6 ± 0.2	12.3 ± 0.3	20.4	15.5
14	60% MeOH	15.1 ± 0.2	13.7 ± 0.3	18.2	14.3
15	40% MeOH	16.5 ± 0.2	—	22.1	18.5
16	30% MeOH	17.0 ± 0.4	—	20.4	17.5
17	20% MeOH	16.1 ± 0.5	—	15.8	13.9
18	CH_3CO_2H	0.0279 ± 0.0010	—	0.047	0.039
19	97% TFE	0.0174 ± 0.0007	—	0.022	0.023
20	90% TFE	0.107 ± 0.004	—	0.126	0.121
21	80% TFE	0.409 ± 0.008	—	0.41	0.38
22	70% TFE	0.898 ± 0.014	—	0.77	0.71
23	60% TFE	1.64 ± 0.05	—	1.15	1.05
24	50% TFE	2.77 ± 0.04	—	1.72	1.55
25	95% Acetone	6.40 ± 0.18	8.27 ± 0.15	2.9	—
26	90% Acetone	12.6 ± 0.2	16.3 ± 0.3	5.8	—
27	80% Acetone	20.3 ± 0.6	20.6 ± 1.0	10.9	—
28	70% Acetone	23.7 ± 0.5	23.4 ± 0.6	15.4	—
29	60% Acetone	25.7 ± 0.5	24.5 ± 0.4	18.9	—
30	50% Acetone	26.1 ± 0.4	23.3 ± 0.6	20.4	—
31	40% Acetone	23.4 ± 0.2	—	21.7	—
32	30% Acetone	20.7 ± 0.5	—	25.6	—
33	20% Acetone	18.4 ± 0.5	—	25.6	—
34	10% Acetone	16.7 ± 0.6	—	18.5	—
35	70% Dioxane	23.4 ± 0.5	26.4 ± 0.7	9.6	—
36	60% Dioxane	28.0 ± 0.7	24.6 ± 0.4	12.7	—
37	50% Dioxane	28.9 ± 0.6	—	18.9	—
38	95% EtOH	5.18 ± 0.05	5.14 ± 0.07	—	—
39	10% EtOH	14.7 ± 0.4	—	—	—
40	100% H_2O	15.8 ± 0.3[j,k]	—	18.1[l]	—

Table 1. (*continued*).

Code	Solvent[b]	$k/10^{-4}$ s^{-1}		$k_{est}/10^{-4}$ s^{-1} [e]	$k_{est}/10^{-4}$ s^{-1} [f]
		A[c]	B[d]		
41	95% MeOH	7.57 ± 0.13	7.49 ± 0.07	—	—
42	50% MeOH	15.9 ± 0.4	—	—	—
43	10% MeOH	15.7 ± 0.3	—	—	—
44	Pr^{i}OH	—	1.87 ± 0.06	—	—
45	Bu^{t}OH	—	1.29[m]	—	—
46	100% TFE	0.0094[n]	—	0.0035[l]	—
47	40% TFE	4.77 ± 0.09	—	—	—
48	30% TFE	8.16 ± 0.23	—	—	—
49	20% TFE	11.9 ± 0.5	—	—	—
50	10% TFE	12.6 ± 0.6	—	—	—
51	95% Dioxane	2.54 ± 0.06	3.26 ± 0.12	—	—
52	90% Dioxane	7.20 ± 0.10	8.47 ± 0.20	—	—
53	80% Dioxane	16.4 ± 0.4	17.3 ± 0.5	8.5[l]	—
54	40% Dioxane	27.8 ± 0.4	—	—	—
55	30% Dioxane	23.2 ± 0.4	—	—	—
56	20% Dioxane	20.4 ± 0.5	—	—	—
57	10% Dioxane	17.4 ± 0.2	—	—	—
58	90 TFE–10E[o]	0.039 ± 0.001	—	—	—
59	80 TFE–20E	0.093 ± 0.003	—	0.36[l]	—
60	70 TFE–30E	0.184 ± 0.005	—	—	—
61	60 TFE–40E	0.323 ± 0.008	—	1.05[l]	—
62	50 TFE–50E	0.536 ± 0.011	—	—	—
63	40 TFE–60E	0.848 ± 0.007	—	2.37[l]	—
64	30 TFE–70E	1.29 ± 0.02	—	—	—
65	20 TFE–80E	1.89 ± 0.03	—	3.16[l]	—
66	10 TFE–90E	2.52 ± 0.04	—	—	—

[a] Concentration of 0.003–0.01 mol dm^{-3}. [b] Solvent prepared on v/v basis at 24.95 °C, except for the TFE–H_2O mixtures which are prepared on a weight-weight basis. [c] Reaction solution prepared by adding concentrated solution of methyl perchlorate (1 cm^3) in dioxane to solvent (49 cm^3) prepared as described in footnote *b*; with associated standard deviations. [d] As for footnote *c*, except that the concentrated solution of methyl perchlorate was in benzene. [e] Using the *l* and *m* values calculated using the data from the first 37 solvents and N_T and Y_{OClO_3} values (see Table 2). [f] As for footnote *e*, but with the values calculated using only the first 24 solvents of the table. [g] With $MeOClO_3$ (0.0086 mol dm^{-3}); with $MeOClO_3$ (0.0034 mol dm^{-3}), a value of 3.15(±0.09) × 10^{-4} s^{-1} was obtained. [h] With $MeOClO_3$ (0.0086 mol dm^{-3}); with $MeOClO_3$ (0.0039 mol dm^{-3}), a value of 8.45(±0.21) × 10^{-4} s^{-1} was obtained. [i] With 2 cm^3 of benzene solution added to 48 cm^3 of MeOH, a value of 6.75(±0.10) × 10^{-4} s^{-1} was obtained. [j] Value with $MeOClO_3$ (0.0035 mol dm^{-3}); with $MeOClO_3$ (0.0086 mol dm^{-3}), a value of 13.0(±0.9) × 10^{-4} s^{-1} was obtained. [k] Values previously reported by other workers are very close to 17.5 × 10^{-4} s^{-1} (refs. 7, 15 and 18). [l] Since the Y_{OClO_3} value is not available, this estimate is obtained as in footnote *e*, but with the Y_{OTs} value used as a substitute. [m] Extrapolated, using the Arrhenius equation, from data at higher temperatures (see Table 3). [n] Initial value, from extrapolation of a plot of log *k* *vs.* extent of reaction; at 40% reaction, integrated value has fallen to 3.3 × 10^{-7} s^{-1}. [o] TFE–ethanol(E) mixtures.

lower rates for the more aqueous solvents, when the stock solution is in benzene, probably reflect the failure of a simple visual inspection to detect small amounts of inhomogeneity.

The appreciably negative entropies of activation (−68 to −96 J K^{-1} mol^{-1}) observed for each of the five solvents in which the specific rates were studied as a function of temperature (Table 3) is consistent with, but does not demand, a bimolecular mechanism for methyl perchlorate solvolysis. Certainly, the values contrast markedly with the usually positive values (−9 to +55 J K^{-1} mol^{-1}) observed[22] for the S_N1 solvolyses of 2-adamantyl perchlorate within these five solvents. The very small accelerations observed on adding tetra-n-butylammonium perchlorate to the methanolysis reaction (Table 4) must also be considered as giving support to the proposal of an S_N2 rather than an S_N1 reaction.

In water, methyl perchlorate has been shown to solvolyse with a slightly positive entropy of activation[7,18] and this was initially considered in terms of an S_N1 mechanism.[18] The observation that ethyl perchlorate hydrolyses only marginally faster than methyl perchlorate rendered such a mechanism highly unlikely.[11] The suggestion of S_N1 character was also attacked on other grounds.[27–29] In our preliminary communication of a portion of these results,[13] we interpreted very low Grunwald–Winstein *m* values [obtained using the one-term form of the equation; *i.e.*, eqn. (1) without the *lN* term] in terms of a traditional S_N2 mechanism rather than an S_N1 mechanism[18] or the subsequently postulated[7,30] S_N2 C^+ (Sneen ion-pair[31]) mechanism (involving rate-determining attack by solvent on a preformed ion pair).

A much clearer picture of the mechanism can be obtained from a treatment in terms of the extended Grunwald–Winstein, eqn. (1). We have carried out analyses of this type for the four possible combinations of N_T and N_{OTs} solvent nucleophilicity scales with Y_{OClO_3} and Y_{OTs} solvent ionizing power scales (Table 2). There is uncertainty as regards the actual values for the N_{OTs} scale, depending upon whether the original[32] m_{OTs} value of 0.30 or the revised[33] value of 0.55 is chosen in the derivation of the N_{OTs} scale from measurements of the specific rates of solvolysis of methyl toluene-*p*-sulphonate. However, provided the *Y* scale for the anionic leaving group resembles the Y_{OTs} values, the *l* value and the correlation coefficient are independent of the value chosen for m_{OTs}, and any error in the m_{OTs} value is reflected in a corresponding error in the *m* value.[33] Therefore, it is not surprising that, when all solvents for which both the *N* and *Y* values for the scales under consideration are known are included in the analysis, the *l* values for methyl perchlorate solvolysis obtained using differing scales are very similar in value. The range of 1.03–1.08 for the *l* value is accompanied by a range of standard deviations of from 0.04–0.10. The correlation coefficients are in the range 0.965–0.974 when Y_{OClO_3} values are used and in the range 0.876–0.936 when Y_{OTs} values are used. The poorer correlations using Y_{OTs} are primarily due to the

Table 2. Correlation of the specific rates of solvolysis of methyl perchlorate,[a] at 24.95 °C, using the extended Grunwald–Winstein equation.[b,c]

Solvents[d]	Scales[e–g]	l	m	c	r[h]
1–37	N_T, Y_{OClO_3}	1.06 ±0.04	0.44 ±0.03	0.16 ±0.19	0.974
1–24	N_T, Y_{OClO_3}	1.02 ±0.03	0.45 ±0.02	0.01 ±0.10	0.994
1–24 26–34	N_{OTs}, Y_{OClO_3}	1.06 ±0.06	0.19 ±0.03	0.14 ±0.22	0.965
1–24	N_{OTs}, Y_{OClO_3}	1.03 ±0.02	0.19 ±0.01	0.01 ±0.07	0.997
1–35	N_T, Y_{OTs}	1.03 ±0.10	0.30 ±0.05	0.44 ±0.40	0.876
1–24	N_T, Y_{OTs}	1.10 ±0.04	0.49 ±0.02	0.07 ±0.13	0.990
1–24 26–34	N_{OTs}, Y_{OTs}	1.08 ±0.07	0.12 ±0.03	0.29 ±0.30	0.936
1–24	N_{OTs}, Y_{OTs}	1.06 ±0.02	0.20 ±0.01	0.04 ±0.07	0.997

[a] From Table 1. [b] Data analysed using $\log(k/k_0) = lN + mY + c$, where c is a constant term. [c] The l, m and c values are quoted with associated standard errors. [d] Using the numbering code of Table 1. [e] The scales of solvent nucleophilicity (N_T or N_{OTs}) and solvent ionizing power Y_{OClO_3} or Y_{OTs}) used in the analysis. [f] Y_{OClO_3} values available only for solvents 1–37 and 44 and 45; however, the N_T values are not available for 44 and 45. [g] Several N_T values obtained by interpolation: 90% EtOH, 0.17; 70% EtOH, −0.18: 50% EtOH, −0.55; 30% EtOH, −0.96; 10% EtOH, −1.32; 90% MeOH, 0.08; 70% MeOH, −0.33; 50% MeOH, −0.71; 30% MeOH, −1.06; 10% MeOH, −1.33; 80% TFE, −2.19; 60% TFE, −1.85; 70% acetone, −0.45; 50% acetone, −0.69; 30% acetone, −0.98; 10% acetone, −1.27; 50% dioxane, −0.66. [h] Correlation coefficient.

Table 3. Specific rates of solvolysis of methyl perchlorate at various temperatures,[a] and enthalpies ($\Delta H^{\ddagger}_{298}$/kJ mol^{-1}) and entropies ($\Delta S^{\ddagger}_{298}$/J K^{-1} mol^{-1}) of activation.[b]

Solvent	T/°C	k/10^{-4} s^{-1}	$\Delta H^{\ddagger}_{298}$	$\Delta S^{\ddagger}_{298}$
MeOH	55.0	80.4 ± 2.3		
MeOH	45.0	32.7 ± 1.3		
MeOH	35.0	17.0 ± 0.3		
MeOH	16.0	2.89 ± 0.05	63.2 ± 1.2[c]	−91.5 ± 4.6[c]
EtOH	55.0	47.8 ± 2.0		
EtOH	45.0	21.9 ± 0.8		
EtOH	35.0	8.69 ± 0.09		
EtOH	16.0	1.37 ± 0.03	69.5 ± 0.8	−76.5 ± 2.5
Pr^{i}OH	55.0	28.7 ± 0.9		
Pr^{i}OH	45.0	12.7 ± 0.3		
Pr^{i}OH	35.0	4.90 ± 0.21		
Pr^{i}OH	16.0	0.67 ± 0.01	73.2 ± 0.8	−68.6 ± 2.5
Bu^{t}OH	55.0	16.9[d]		
Bu^{t}OH	45.0	7.05[d]		
Bu^{t}OH	35.0	3.27[d]	66.1 ± 2.1	−95.7 ± 7.1
80% EtOH	45.0	53.4 ± 0.9		
80% EtOH	35.0	22.1 ± 0.6		
80% EtOH	16.0	3.15 ± 0.05	72.2 ± 1.0	−61.6 ± 3.4

[a] Solutions prepared from 1 cm^3 of concentrated benzene solution and 49 cm^3 of solvent; with the associated standard deviations; the value at 24.95 °C (not available for Bu^{t}OH) was also used (from Table 1) in calculating the activation parameters. [b] With associated standard errors. [c] Ref. 19 reports values of 65.9 kJ mol^{-1} for $\Delta H^{\ddagger}$ and −87.2 J K^{-1} mol^{-1} for $\Delta S^{\ddagger}$. [d] In each run, the integrated rate coefficients increased slightly with extent of reaction and initial values were obtained by extrapolation.

Table 4. Effect of added Bu$^n_4$NClO$_4$ upon the specific rates of methanolysis[a,b] of methyl perchlorate, at 24.95 °C.

[Bu$^n_4$NClO$_4$]/ 10^{-2} mol dm^{-3}	k/10^{-4} s^{-1}
0.50	6.89
1.00	6.94
2.00	7.10
4.00	7.39
6.00	7.54
8.00	7.74

[a] A 0.0086 mol dm^{-3} solution of methyl perchlorate in a solvent formed by mixing 1 cm^3 of benzene with 49 cm^3 of methanol. [b] Standard deviations within the range of 0.8–1.9% of reported value.

scale not being suitable for a perchlorate leaving group in aqueous acetone and aqueous dioxane systems;[22] when these two types of solvent system are omitted, the range of l values changes only slightly (1.02–1.10) but the range of standard deviation (0.02–0.04) and of correlation coefficient (0.990–0.997) reflect considerably improved correlation.

The m values vary appreciably (Table 2) depending upon whether N_{OTs} or N_T values are used. Using N_{OTs} and Y_{OClO_3}, the m value of 0.19 for both full and reduced sets of solvents converts to a value of $m + 0.25\,l$ if the revised N_{OTs} scale (based on a m_{OTs} value of 0.55) is used.[33] This value of 0.45 is then in excellent agreement with the value of 0.44 obtained using the N_T scale. Similarly, the values of 0.12 and 0.20 for m, obtained using N_{OTs} and Y_{OTs}, are corrected to values of 0.39 and 0.47, in good agreement with the values of 0.30 and 0.49 obtained using N_T and Y_{OTs} scales. The good agreement between the use of the N_T scale and the revised N_{OTs} scale supports the development and use of the modified (N'_{OTs}) scale.

The l value of marginally greater than unity indicates an extent of nucleophilic participation essentially identical to that for the *S*-methyldibenzothiophenium ion[25] or methyl toluene-*p*-sulphonate.[32] The m value of 0.44 using N_T and Y_{OClO_3} values suggests slightly less dependence on solvent ionizing power than for methyl *p*-toluenesulphonate solvolysis. The analysis indicates formation of an activated complex very similar in character to that formed during methyl toluene-*p*-sulphonate solvolysis. Although Abraham and McLennan supported the idea of an S_N2 mechanism in preference to S_N2 C$^+$ [7,30] or S_N1,[18] they postulated a relatively loose transition state with an unusually large amount of bond breaking.[27] This view of the activated complex structure is not supported by the large l and relatively small m values obtained in this study.

A different model for the activation process during the hydrolysis of methyl perchlorate was presented by Kurz.[15] He considered the activation process to involve a change in the solvation of a preassociated water–methyl perchlorate pair. In the transition state, relative to the internal charge distribution, the solvation was more similar to its condition in the products. In particular, there was considered to be little or no charge development on the oxygen of the attacking water molecule. Our finding of a large sensitivity towards solvent nucleophilicity, with water behaving as would be expected, argues against a model of this type. We have discussed elsewhere[25] possible defects in the detailed mechanisms used by Kurz in his analysis of solvent deuterium isotope effects during methyl transfers to water and alcohols.

It is of interest to check the rates calculated using the determined l and m values against those actually observed. This is to see not only how good the predictions are but also to search for solvent systems exhibiting a poor agreement between calculated and experimental values, indicating either experimental error or, more likely, some unusual mechanistic characteristic in those solvents. The comparison is commonly done by plotting $\log(k/k_0)$ *vs.* $lN + mY$. In the present case, however, the rates of solvolysis are very similar for the majority of the solvents, with just a few solvents (acetic acid and solvents rich in TFE) reacting appreciably slower; accordingly, a better (and also more sensitive) approach is to compare, directly, the experimental specific rates with those estimated from eqn. (1) (Table 1).

For the first 37 solvents of Table 1, using N_T and Y_{OClO_3} values, together with the appropriate l and m values (Table 2), the agreement between calculated and experimental rates is very good. Reproduction is within a factor of three, in all cases, with the poorest agreement being for solvolysis in aqueous acetone and aqueous dioxane. When these two solvent systems are omitted (use of first 24 solvents), the agreements between calculated and experimental specific rates is then always within a factor of two; in the usual logarithmic comparisons, such deviations would correspond to less than 0.3 units.

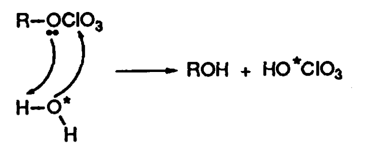
For several additional solvents (code numbers higher than 37), the known N_T values can be combined (in the absence of Y_{OClO_3} values) with Y_{OTs} values.[24] Retaining the l and m values used in the analysis of the first 37 solvents, the calculated and experimental rates agree within a factor of four.

In these comparisons of calculated and experimental rates, it is especially pleasing to see that the calculated specific rates, for a given aqueous–organic system, pass through a maximum in the region of high water content in a very similar way to that shown by the experimental specific rates.[14] Overall, in view of the fact that the relative specific rates are determined as the sum of usually opposing nucleophilicity and ionizing power considerations, the ability to estimate experimental rates with fairly high precision demonstrates the usefulness of the extended Grunwald–Winstein equation in the correlation of the specific rates of solvolyses proceeding by the S_N2 mechanism. Indeed, it is amusing to see that the only slightly different specific rate of hydrolysis of methyl perchlorate in pure water relative to solvolysis in 80% ethanol (standard solvent) involves a large accelerative influence of increased solvent ionizing power coupled with a large, and almost compensating, decelerative influence of reduced nucleophilicity: a mY_{OClO_3} term of $+1.79$ is coupled with an lN_T term of -1.49.

For an S_N2 reaction, it has been shown previously that for a limited range of a given aqueous–organic solvent mixture, the variation of specific rate with solvent composition can often be correlated against only solvent ionizing power, using the simple Grunwald–Winstein equation.[34,35] This is because a linear relationship often holds between the N and Y scales.[26,36] For consideration of methyl perchlorate solvolysis in 100–40% aqueous ethanol, it is found that the N_T values are linearly related (correlation coefficient of 0.987) to the Y_{OClO_3} values with a slope of -0.27. We can estimate[26] the experimental m value of the simple treatment in terms of the l and m values (Table 2) of the extended (two-term) treatment as ($0.44 - 0.27 \times 1.06$). Indeed, this value of 0.15 is identical to the slope of the linear plot (correlation coefficient of 0.981) obtained by plotting log k values *vs.* Y_{OClO_3} values for this concentration range.

The question needs to be addressed as to whether it is possible that, in some cases, nucleophilic attack occurs not at the carbon but at the chlorine of the perchlorate ion with expulsion of the methoxy group (probably with a concentrated transfer of a proton from the hydroxylic attacking species such that it would leave as a methanol molecule). For attack by water, the products would be identical to those for attack at the carbon. However, attack by alcohols would not develop acid and would correspond to a transesterification. In particular, such an attack in the methanolysis of methyl perchlorate would be a symmetrical exchange reaction. Since reactions in alcohols develop acid at the rate which is expected based upon reaction in aqueous media, we can rule out any appreciable attack at the chlorine.

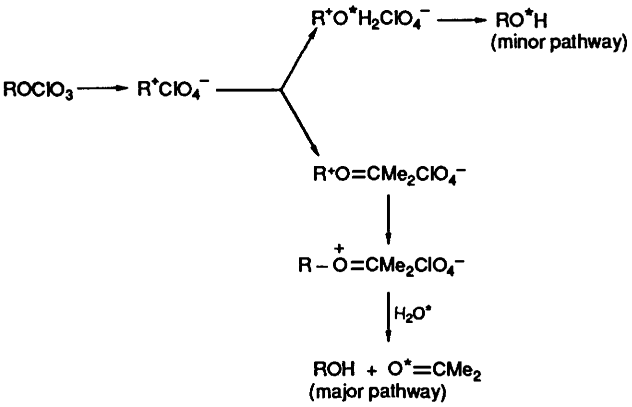
Attack at chlorine has been proposed, however, for solvolysis of secondary perchlorate esters based upon the tetracyclo-[5.3.0.0^{2,5}.0^{3,8}]decane skeleton.[3,20] Reaction in boiling acetone containing 3–5% H_2O, with the H_2O appreciably labelled with ^{18}O, led to alcohol with no detectable incorporation of the ^{18}O. It was concluded that the attack was as in reaction (3). We suggest that a more likely explanation is that (as with



(3)

(3)

2-adamantyl perchlorate[22]) the reactions are S_N1 in character with capture of the cation at the solvent-separated ion pair stage. In this way involvement of the 95–98% acetone rather than the 3–5% H_2O is not unreasonable. This may be more favourable than for solvolysis of other types of esters because of the observation that the perchlorate ion is unusual in being better solvated by a dipolar aprotic solvent than by water.[37] In particular if the mechanics of the solvent separation involve rotation of a molecule solvating the anion to a position between the ions, solvation by acetone would lead to this molecule assuming the ideal position for reaction with the cation. The proposed scheme can be represented as in Scheme 1.



Scheme 1.

Indirect support for Scheme 1 comes from the observation of predominantly tetrazole formation (involving capture of an intermediate acetonitrilium ion by azide ion), accompanied by only small amounts of 1-adamantyl azide, in the reaction of 1-adamantyl arenesulphonates with appreciable concentrations of azide ion in acetonitrile.[38] Also, we have proposed previously[22] that the perturbation of the alcohol : ether ratio for solvolysis of adamantyl derivatives in aqueous ethanol which was observed[39] upon adding acetone was the result of intervention by acetone molecules followed by further reaction of an intermediate oxonium ion. The labelling experiment could be done so as to give an unambiguous answer as to whether the attack is at chlorine or carbon by labelling the oxygens of the perchlorate group rather than the oxygen of the water. Then, the pathway of reaction (3) will lead to label being retained in the alcohol, but either pathway of Scheme 1 (or any other scheme involving loss of perchlorate ion) will lead to unlabelled alcohol.

Experimental

Materials.—The purifications of acetone, dioxane, ethanol and methanol were as previously described.[40] The purifications of acetic acid[41] and 2,2,2-trifluoroethanol[42] were also performed by previously reported procedures. The propan-2-ol and t-butyl alcohol were refluxed with CaH_2 and glass wool (to prevent bumping) for several days, followed by distillation through a fractionating column with exclusion of moisture. Benzene was dried over $CaCl_2$ for one week and distilled from Linde 4A molecular sieves. Except for dioxane (2×10^{-3} mol dm^{-3} H_2O), all solvents were less than 10^{-3} mol dm^{-3} in water (Karl Fischer reagent). Reagent grade methyl iodide was distilled through a 60 cm fractionating column and stored in the dark over a drop of mercury. Silver perchlorate (G. F. Smith Chem. Co., anhydrous) was recrystallized from dry benzene and, immediately before its use in the synthesis of methyl perchlorate, it was dried in a vacuum drying oven (12 mmHg, 136 °C) for 24 h.

The preparation of a benzene solution of methyl perchlorate has been described previously;[1] the solution was stable for at least 6 months. A typical procedure for preparing a solution in dioxane involves adding dry silver perchlorate (2 g) to dioxane (40 cm^3), followed by a 5% excess of methyl iodide. After stirring for 8–10 h, the solution was filtered and the filtrate passed through a small column of Linde 4A molecular sieves. Unlike the solution in benzene, the dioxane solution slowly deteriorated on standing, probably due to methylation of the solvent, and stock solutions in dioxane were used within 10 h of their preparation.

Kinetic Procedures.—The stock solution of methyl perchlorate in dioxane or benzene and 49 cm^3 of the solvent to be investigated were allowed to separately equilibrate at the required temperature. A portion of the stock solution (1 cm^3) was then transferred to the solvent. After a few minutes for reequilibration of the temperature, an aliquot (5 cm^3) was removed as the zero point, followed by other aliquots at appropriate time intervals, and after at least ten half lives an aliquot was removed for determination of the infinity titre. For the slower runs ($k < 10^{-5}$ s^{-1}), the time to V_∞ was reduced by addition of an aliquot (5 cm^3) to methanol (5 cm^3) or, in the case of acetic acid, by heating an aliquot (5 cm^3) in a sealed tube to 80 °C.

The titration procedure for runs in acetic acid and the calculation of the integrated first-order rate coefficients were as previously described.[26] For other runs, either of two procedures was used to quench the reaction prior to titration. The reaction could be quenched by adding the removed aliquots to a neutral saturated solution of LiCl in acetone (30 cm^3; *ca.* 6.6 g dm^{-3}). The large excess of chloride ion rapidly converted unchanged methyl perchlorate to much less reactive methyl chloride and the acid previously developed was titrated against a standardized solution of sodium methoxide in methanol to a Lacmoid (resorcinol blue) endpoint. Alternatively, the reaction was quenched by addition of the removed aliquots to neutral acetone (20 cm^3) cooled in a solid CO_2–acetone slush, followed immediately by the titration previously described. For runs in the presence of tetra-n-butylammonium perchlorate, the required concentration of salt was initially present in the 49 cm^3 of methanol.

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