

MECHANISM OF METHYL PERCHLORATE SOLVOLYSIS

IN HYDROXYLIC SOLVENTS<sup>1</sup>

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Recent interpretations<sup>2,3</sup> of the hydrolysis kinetics of methyl perchlorate in terms of an  $S_N2C^+$  (Sneen Ion-Pair<sup>4</sup>) mechanism have been vigorously attacked<sup>5</sup>. The current interest in methyl perchlorate solvolysis prompts us to report a study we have made of the solvolysis kinetics in methanol, ethanol, isopropanol, *t*-butanol, and 80% aqueous ethanol. Methyl perchlorate was prepared as a solution in benzene by the homogeneous reaction of methyl iodide with silver perchlorate and removal of precipitated silver iodide by filtration<sup>6,7</sup>. The reactant solution was 98% of the appropriate solvent and 2% benzene. For methanolysis, at 25.0°, it was shown that the specific rate with 2% benzene ( $6.80 \times 10^{-4} \text{sec.}^{-1}$ ) was little effected ( $6.75 \times 10^{-4} \text{sec.}^{-1}$ ) by a change to 4% benzene and, presumably, the rates in the pure solvents would vary little from those observed with 2% benzene present.

For each solvent a study was made at several temperatures. Analysis was after addition to acetone saturated with lithium chloride, so as to rapidly convert unreacted methyl perchlorate to unreactive methyl chloride, and the acid previously developed was titrated against methanolic sodium methoxide using Lacmoid (resorcinol blue) as indicator. The first-order rate coefficients are reported, together with the enthalpies and entropies of activation, within Table I.

The data for the methanolysis are in good agreement with those previously reported by Koskikallio<sup>8</sup>. Data which have been reported<sup>3,9</sup> for hydrolysis in 100% water are also included within the Table.

Using the first-order rate coefficients measured at 25.0°, (in the case of *t*-butanol extrapolated to 25.0°) together with the value previously reported<sup>3,9</sup> for hydrolysis in pure water and taking  $\gamma$  values from the literature<sup>10</sup>, a Grunwald-Winstein  $mY$  plot can be constructed. The points can be very well represented by two straight lines with a discontinuity at the point for methanol; this is where the solvent system changes from pure alcohols ( $\bar{m}=0.33$ ) to aqueous solvents ( $\bar{m}=0.11$ ).<sup>11</sup>

TABLE I

First-order Rate Coefficients<sup>a</sup> for Solvolysis of Methyl Perchlorate at Various Temperatures (°C) and Enthalpies and Entropies of Activation<sup>b</sup> at 298°K.

Solvent <sup>c</sup>	$10^4 k_1 (\text{sec.}^{-1})$					$\Delta H^\ddagger (\text{kcal/mol})$	$\Delta S^\ddagger (\text{e.u.})$
	16.0°	25.0°	35.0°	45.0°	55.0°		
H <sub>2</sub> O	(17.4 <sup>d</sup> , 17.9 <sup>e</sup> )					21.5 <sup>d</sup>	+0.9 <sup>d</sup>
80%EtOH	3.15	8.36	22.1	53.4		17.2±0.3	-14.8±0.9
MeOH <sup>f</sup>	2.89	6.80	17.0	32.7	80.4	15.2±0.3	-22.0±1.1
EtOH	1.37	3.42	8.90	21.9	47.8	16.7±0.2	-18.4±0.6
i-PrOH	0.67	1.87	4.90	12.7	28.7	17.6±0.2	-16.5±0.6
<u>t</u> -BuOH		(1.29) <sup>g</sup>	3.27	7.05	16.9	15.9±0.5	-23.0±1.7

<sup>a</sup>Standard deviations, calculated for each run, in range of 1 to 3% of value. <sup>b</sup>With associated standard deviations. <sup>c</sup>Solvent consisted of 98% of that listed and 2% benzene (by volume). <sup>d</sup>From ref. 3. <sup>e</sup>From ref. 9. <sup>f</sup>Ref. 8 reports an enthalpy of activation of 15.7 kcal/mol. and an entropy of activation of -20.8 e.u. <sup>g</sup>From extrapolation of the data obtained above the melting point.

Other solvolyses of methyl derivatives for which  $m$  values have been reported<sup>12</sup> include methyl bromide (0.26) and methyl benzenesulfonate (0.23). The values in the present study are consistent with a bimolecular mechanism involving nucleophilic attack, such as was assumed<sup>12</sup> for the previously studied methyl derivatives.

A suggestion that methyl perchlorate hydrolysis is  $S_N1$  in character<sup>9</sup>, discredited on the basis of a  $\text{MeOClO}_3/\text{EtOClO}_3$  rate ratio of close to unity<sup>13</sup>, was later modified to a suggestion of  $S_N2C^+$  character<sup>2,3</sup>. Application of the Hammond postulate requires the transition state for the second step to closely resemble the high-energy ion-pair<sup>3,14</sup>. It follows that there would be little bond-making to the nucleophile in the transition state for its attack and, indeed, since the methyl carbonium ion formation will involve considerably more energy than corresponding formation of a t-butyl carbonium ion, one can even visualize a greater dependence on solvent ionizing power for  $S_N2C^+$  reaction proceeding through a methyl carbonium ion than for  $S_N1$  reaction proceeding through a t-butyl carbonium ion; *i.e.*, an  $m$  value of greater than unity. Certainly, it is difficult to rationalize extremely low values for  $m$  in terms of an  $S_N2C^+$  mechanism. For example, solvolyses of  $\gamma$ -*p*-toluylsulfonyl substituted tertiary allylic systems in aqueous alcohols, for which

$S_N2C^+$  type mechanisms have been reasonably postulated<sup>15</sup>, have  $\underline{m}$  values considerably higher than the values of 0.11 for methyl perchlorate and in the range of 0.46 to 0.69.

In the present study, it is found that in going from pure alcohols, of relatively low ionizing power, to 80% ethanol and pure water the  $\underline{m}$  value shows a marked reduction in value as the solvent ionizing power ( $\gamma$  value) increases. This strongly suggests that, in these highly ionizing solvents, considerations of reduced nucleophilicity are almost as important as increases in solvent ionizing power and this requires appreciable bonding of the nucleophile to the  $\alpha$ -carbon at the transition state. This is contrary to what one would predict for an  $S_N2C^+$  mechanism but consistent with a "classical"  $S_N2$  mechanism.

A consideration in terms of selectivity-stability considerations<sup>16,17</sup> leads to identical conclusions. Attack on a high-energy methyl carbonium ion should show low selectivity between attacking nucleophiles and ionizing power considerations should be of prime importance, leading again to a prediction of a high  $\underline{m}$  value. A detailed consideration of the observed  $\underline{m}$  values would not be justified since the Grunwald-Winstein equation strictly applies to only the rates of processes paralleling the solvolyses of *t*-butyl chloride. While values considerably below unity are taken as evidence for the operation of both nucleophilic and electrophilic assistance, analyses on the basis of two-term equations have had only limited success<sup>18</sup>.

For methanolysis, a study was made of the effect of added tetra-*n*-butylammonium perchlorate. In contrast to the large effect of this salt upon methanolyses in benzene as solvent<sup>6</sup>, concentrations of up to 0.08  $\underline{M}$  produced only very modest rate increases (Table II). Although salt effects

TABLE II

Effect of Tetra-*n*-butylammonium Perchlorate Addition Upon the First-order Rate Coefficients for Methanolysis<sup>a</sup> of Methyl Perchlorate at 25.0°.

[ <i>n</i> -Bu <sub>4</sub> NC10 <sub>4</sub> ], $\underline{M}$ :	0.000	0.005	0.010	0.020	0.040	0.060	0.080
$10^4 k_1$ (sec. <sup>-1</sup> ) :	6.80 <sup>b</sup>	6.89	6.94	7.10	7.39	7.54	7.74

<sup>a</sup>In 98% methanol-2% benzene (by volume). <sup>b</sup>From Table I.

are notoriously difficult to analyze in this regard<sup>5</sup>, these very small salt effects would appear to be more consistent with an  $S_N2$  than an  $S_N2C^+$  mechanism.

In conclusion, the solvolysis kinetics of methyl perchlorate in a wide variety of hydroxylic solvents are better rationalized in terms of an  $S_N2$  mechanism than in terms of the recently proposed<sup>2,3</sup>  $S_N2C^+$  type mechanism for these processes.

## REFERENCES AND NOTES

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