Perchlorate-ion Catalysis in the Methanolysis of Methyl Perchlorate in Benzene

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SOLUTIONS of methyl perchlorate[1] in benzene at 25·0°, even in the presence of 0·56 M-phenol, are unchanged during several months; the lack of aromatic methylation strongly suggests the absence of methyl carbonium ion development. Reaction with added methanol can be conveniently measured in terms of acid development:

$$MeOClO_3 + MeOH \rightarrow MeOMe + HOClO_3$$

A fundamentally bimolecular process was indicated by the observation of a very pronounced second-order component (rate coefficient of 0·67 mol.$^{-1}$ sec.$^{-1}$) upon addition of small amounts of sodium methoxide to a solvolysis in 98% methanol (by volume). Prior to a decrease at higher concentrations, the kinetic order in methanol is, from 0·07M- to 0·4M-methanol, approximately 2·3. Addition of phenol led to a deceleration; the effect upon the initial first-order rate coefficient with respect to 0·040 M-methyl perchlorate in its reaction with 0·100 M-methanol at 25·0° is indicated below:

[PhOH]:	0·000	0·028	0·056	0·112	0·224	0·448	0·896
$10^8 k_1$(sec.$^{-1}$):	9·2	7·8	6·9	5·3	4·1	3·0	2·7

The deceleration can best be understood in terms of a neutralization of the nucleophilic capacity of methanol molecules by mixed intermolecular hydrogen bonding of the type previously observed in carbon tetrachloride.[2] This deceleration is in contrast to the acceleration which was observed when triphenylmethyl chloride was the substrate.[3,4]

Despite the contrary responses to the addition of phenol, the order in methanol, within the concentration range for which the two studies overlap, is only slightly less for attack upon methyl perchlorate than for attack upon triphenylmethyl chloride.[4] Emphasis has previously been placed upon electrophilic assistance to the nucleophilic substitution[5] and it appears that the possibility of placing several methanol molecules within the transition state through a nucleophilic attack by hydrogen-bonded methanol polymers has been overlooked; attack of this type would allow a favourable dispersal of the positive charge developing upon the initially neutral nucleophile.

The methanolysis was found to be subject to powerful catalysis by added tetra-n-butylammonium perchlorate ($\mathrm{Bu^n_4NClO_4}$) and the catalyzed reaction was of one-half order in the addendum.

TABLE. *Effect of added tetra-n-butyl ammonium perchlorate upon the initial specific rate of reaction,* k_1, *of methyl perchlorate* (0·04 M) *with methanol* (0·1 M) *in benzene at* 25·0°

$10^3\,[\mathrm{Bu^n_4NClO_4}]$	0·000	0·000	0·100	0·250	0·500	1·00	2·00
$10^8\,k_1(\mathrm{sec.}^{-1})$:	9·12	9·15	24·2	34·2	44·2	57·0	73·0
$b^a\,(\mathrm{M}^{-1/2})$:	—	—	**164**	**172**	**172**	**166**	**157**

[a] Calculated from $k_1 = k_1^0(1 + b[\mathrm{Bu^n_4NClO_4}]^{\frac{1}{2}})$, where k_1 is the specific rate for appropriate $[\mathrm{Bu^n_4NClO_4}]$ and k_1^0 is the specific rate at zero $[\mathrm{Bu^n_4NClO_4}]$.

Not only the form but also the actual magnitude of the catalysis parallels very closely that previously observed for the methanolysis of triphenylmethyl chloride.[4] A coefficient *b* (see footnote to Table) calculated from the somewhat less precise data available for the reaction of triphenylmethyl chloride under identical conditions[4] is either of value $134 \pm 14\ \mathrm{M}^{-1/2}$ for $[\mathrm{Bu^n_4NClO_4}]$ up to 2×10^{-4} M falling off to $94\ \mathrm{M}^{-1/2}$ at 2×10^{-3} M (neglecting catalysis by adventitious acid) or the corresponding values are $199 \pm 21\ \mathrm{M}^{-1/2}$ falling to $139\ \mathrm{M}^{-1/2}$ (assuming acid and $\mathrm{Bu^n_4NClO_4}$ catalyses are additive[4]).

It has been suggested[6] that the origin of the closely parallel $\mathrm{Bu^n_4NClO_4}$ catalysis, observed with triphenylmethyl chloride as substrate, lies in Winstein's "special salt effect". An ion-pair exchange between methyl perchlorate and $\mathrm{Bu^n_4N}$-$\mathrm{ClO_4}$ would be symmetrical and could not possibly lead to an acceleration. One alternative scheme, consistent with the observed kinetic pattern, involves interaction between $\mathrm{Bu^n_4NClO_4}$ ion-pairs and methanol molecules to give a species with increased nucleophilicity at the methanolic oxygen:

$$\mathrm{Bu^n_4N^+ClO_4^-} + \mathrm{MeOH} \rightleftharpoons \mathrm{Bu^n_4N^+} + (\mathrm{MeOH} \cdots \mathrm{OClO_3})^-$$

We are currently investigating related systems in an attempt to determine whether an interaction with methanol, rather than with some intermediate derived from the substrate,[6,7] can indeed be the origin of perchlorate-ion catalysis to methanolyses in benzene.

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