Perchlorate Esters. Part 8.[1] Kinetics and Mechanism of the Methanolysis of Methyl Perchlorate in Benzene

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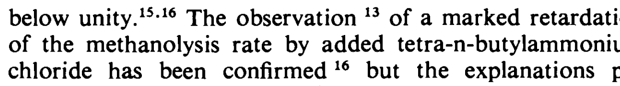
Methyl perchlorate reacts with 0.07—0.4M-methanol in benzene with a kinetic order of *ca.* 2.3 in methanol. The reaction is accelerated by addition of nitromethane but, in contrast to the corresponding methanolysis of triphenylmethyl chloride, decelerated by added phenol. Small concentrations of tetra-n-butylammonium perchlorate cause very large increases in the methanolysis rate. The mechanism is essentially S_N2 in character but subject to general-base catalysis ,either by additional methanol molecules or by perchlorate ion. With phenol present, deactivation of methanol molecules by hydrogen bonding outweighs any electrophilic assistance rendered to perchlorate-ion departure. An alternative mechanism for the previously studied methanolysis of triphenylmethyl chloride in benzene is presented; unlike previous proposals, this mechanism is compatible with the retardation of the methanolysis by moderate concentrations of tetra-n-butylammonium chloride.

Studies of nucleophilic substitutions in the low polarity solvent benzene have been largely confined to studies of Menschutkin reactions [2–6] and to extensive studies of the reactions of triphenylmethyl chloride with various nucleophiles,[3,7–10] including methanol.[11–17] Considerable controversy has surrounded the studies of the methanolysis of triphenylmethyl chloride. It was after a study of this system that Swain proposed the 'Push–Pull' termolecular mechanism for nucleophilic substitutions [11] [reaction (1)]. Hughes *et al.*[13] later showed that the order in methanol is not constant at a value of 2 but varies considerably with concentration, reaching a value of 3 at high (*ca.* 0.5M) concentrations. However, their claim that the order in methanol fell to zero at low concentrations was later shown to be in error and even at very low methanol concentrations the order in methanol does not fall below unity.[15,16] The observation [13] of a marked retardation of the methanolysis rate by added tetra-n-butylammonium chloride has been confirmed [16] but the explanations put forward have been attacked [15,18] and, if interaction is indeed with a $Ph_3C^+Cl^-$ ion pair, it is difficult to see how the aspects of a symmetrical exchange, requiring return to an identical ion-pair, can be avoided. It would appear that no satisfactory explanation of this retardation has been presented. The powerful catalysis of the methanolysis by added tetra-n-butylammonium perchlorate [13,17] was reasonably explained in terms of an anionic exchange,[14] essentially identical to the Winstein special salt effect,[18] and the retardation of this catalysis by added chloride salt can then be considered as a further example of common-ion retardation of the special salt effect (induced common ion effect).



$$\underset{\mathrm{H}}{\overset{\mathrm{Me}}{\mathrm{O}}}\;\mathrm{Ph_3C{-}Cl}\cdots\mathrm{H{-}}\underset{\mathrm{Me}}{\mathrm{O}} \longrightarrow \mathrm{Me}\underset{\mathrm{H}}{\overset{+}{\mathrm{O}}}\mathrm{CPh_3} + (\mathrm{ClHOMe})^-$$

(1)

Triphenylmethyl derivatives favour reaction by ionization mechanisms because of the large resonance stabilization of the carbocation formed and the appreciable steric hindrance to a classical S_N2 attack.[19] The other extreme can be represented by methyl derivatives, where the carbenium ion formed would be of extremely high energy [20] and steric hindrance to S_N2 attack is minimized. Indeed, studies of solvolyses in hydroxylic solvents strongly indicate that, even in solvents of relatively high polarity and low nucleophilicity, a classical S_N2 mechanism is operating.[21] Reaction of methyl halides with methanol in benzene would be extremely slow [3] and we have chosen to study the methanolysis of methyl perchlorate, containing a leaving group that is over 10^3 times better than iodide for reaction with *NN*-dimethylaniline in benzene.[6] A further point of interest in choosing the perchlorate ester is that, even if ionization to an ion-pair was to occur, the Winstein special salt effect cannot operate because the anionic exchange following tetra-n-butylammonium perchlorate addition would now be symmetrical. Any observed catalysis would require an explanation differing from that proposed for the methanolysis of triphenylmethyl chloride.

The major experimental difficulties in the study of triphenylmethyl chloride methanolysis involved a strong autocatalysis by the hydrogen chloride produced and the establishment of an early equilibrium.[11,13] In the methyl perchlorate reaction no autocatalysis or equilibrium is observed and the reaction proceeds smoothly to completion without the need to add pyridine or other base.[15,16] A kinetic study of the methanolysis of methyl perchlorate in benzene, including the effects of addenda, is reported and discussed. Also, an alternative mechanism, consistent with all major observations, is put forward for the corresponding methanolysis of triphenylmethyl chloride.

Results

All the kinetic studies were carried out in benzene as solvent at 25.0 °C.

Methanolysis of Methyl Perchlorate.—For a 0.100M-methanol concentration, the specific rate of reaction of methyl perchlorate (0.01—0.08M) was independent of its concentration (Table 1). It was found (Table 1) that the specific rate of reaction of methyl perchlorate (0.0400M) increases dramatically with methanol concentration (0.04—19.7M). The order in methanol (slope of the plot of Figure 1) varies from *ca.* 2.3 in the 0.07—0.4M-methanol range to *ca.* 1.2 at the higher methanol concentrations. However, at the upper level (19.7M), the solvent is *ca.* 80% methanol and the orders above *ca.* 0.4M-methanol will not be of any direct significance as regards a study in benzene as solvent.

Effect of Molecular Addenda upon the Methanolysis Rate.—A study has been made, with 0.0400M-methyl perchlorate and 0.100M-methanol, of the effect of added phenol ($\leqslant$0.9M) and

Table 1. Initial specific rates, k_1, for the methanolysis of 0.0400M-methyl perchlorate in benzene at 25.0 °C

[MeOH]/M	0.040	0.070	0.100 [a]	0.150	0.200	0.300	
10^6k_1/s^{-1}	~0.009	0.041 [b]	0.092 [c]	0.213	0.415	1.13 [c]	
[MeOH]/M	0.400	0.500	0.800	1.00	1.20		
10^6k_1/s^{-1}	2.22	3.47	8.15	11.9	15.3		
[MeOH]/M	1.80	2.38	3.50	5.00	10.0	15.0	19.7
10^6k_1/s^{-1}	29.8	40.4	67.9	101	238	386 [c]	542 [c]

[a] With [MeOClO$_3$] 0.010, 0.020, 0.060, and 0.080M, values of 10^6k_1/s^{-1} are 0.089, 0.092, 0.094, and 0.097, respectively. [b] Average of three determinations (0.041, 0.041, 0.040). [c] Average of two closely agreeing determinations.

Table 2. Effect of added phenol or nitromethane upon initial specific rates, k_1, for reaction of 0.0400M-methyl perchlorate with 0.100M-methanol in benzene at 25.0 °C

[PhOH]/M	0.000	0.028	0.056	0.112	0.224	0.448 [a]	0.896
10^8k_1/s^{-1}	9.2	7.8	6.9	5.3	4.1	3.0	2.7
[CH$_3$NO$_2$]/M	0.000	0.100	0.200	0.400	0.900	1.40 [b]	
10^8k_1/s^{-1}	9.2	10.7	12.2	15.9	24.6	35.7	

[a] In the absence of methanol, no acid production during 40 days. [b] In the absence of methanol, a background initial specific rate of 0.20 × 10^{-8} s^{-1} is observed.

Table 3. Effect of added tetra-n-butylammonium perchlorate (TNBAP) upon the initial specific rate of reaction, $k_1{}^p$, of 0.0400M-methyl perchlorate with 0.100M-methanol in benzene at 25.0 °C

10^3[TNBAP]/M	0.000	0.100	0.250	0.500	1.00	2.00
$10^8k_1{}^p$/s^{-1}	9.2	24.2	34.2	41.3	57.0	73.0
b [a]/l$^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$		164	172	158	166	157

[a] Calculated from $k_1{}^p = k_1{}^0(1 + b[\text{TNBAP}]^{\frac{1}{2}})$, where $k_1{}^p$ is the specific rate for the appropriate [TNBAP] and $k_1{}^0$ is the specific rate in its absence.

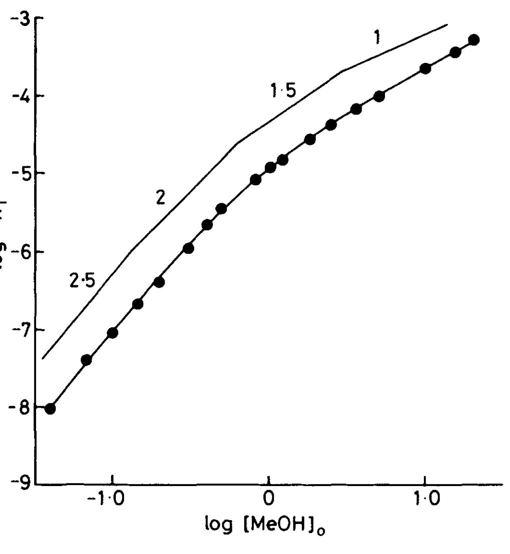


Figure 1. Effect of concentration of methanol on the initial specific rate (k_1/s^{-1}) of its reaction with 0.0400M-methyl perchlorate in benzene at 25.0 °C. Plot of the logarithm of the first-order rate constant with respect to methyl perchlorate *versus* the logarithm of the methanol concentration. The upper series of straight lines show theoretical slopes for kinetic orders of 1, 1.5, 2, and 2.5 with respect to methanol

nitromethane (≤ 1.4M). The inhibiting effect of added phenol and the accelerating effect of added nitromethane are illustrated in Table 2.

Table 4. Effect of methanol concentration upon the initial specific rate, $k_1{}^p$, of methanolysis of 0.0400M-methyl perchlorate in the presence of 5.00 × 10^{-4}M-tetra-n-butylammonium perchlorate in benzene at 25.0 °C

[MeOH]/M	0.040	0.070	0.100	0.170
$10^6k_1{}^p$/s^{-1}	0.127	0.256	0.413	0.782
[MeOH]/M	0.250	0.500	1.00	2.50
$10^6k_1{}^p$/s^{-1}	1.42	4.42	13.0	43.6
[MeOH]/M	5.00	10.0	18.7	
$10^6k_1{}^p$/s^{-1}	104.0	247.0	500.0	

Effect of Added Tetra-n-butylammonium Perchlorate (TNBAP) upon the Methanolysis Rate.—Small concentrations (≤0.002M) were found to have a marked accelerative effect upon the reaction of 0.0400M-methyl perchlorate with 0.100M-methanol. The kinetics were found to follow the equation given in equation (2), where $k_1{}^p$ and $k_1{}^0$ are the

$$k_1{}^p = k_1{}^0(1 + b[\text{TNBAP}]^{\frac{1}{2}}) \qquad (2)$$

specific rates of reaction of methyl perchlorate in the presence and absence of added salt, respectively. Specific rates and b values are presented in Table 3. The effect of varying the methanol concentration at constant TNBAP (5 × 10^{-4}M) and methyl perchlorate (0.0400M) concentrations is reported in Table 4.

Effect of Added Sodium Methoxide upon the Methanolysis in a Solvent approaching Pure Methanol.—A marked increase in the specific rate of methanolysis of methyl perchlorate was observed upon addition of moderate (<0.02M) concentrations of sodium methoxide (Table 5). The rate increased linearly

Table 5. Influence of sodium methoxide upon the specific rate of solvolysis of methyl perchlorate in methanol at 25.0 C° [a]

10^3[MeOClO$_3$]/M	3.80	3.80	3.80	3.80	3.80
10^3[MeONa]/M	0.00	1.95	3.90	5.85	7.80
10^3k_1/s^{-1}	0.58 [b]	1.73	3.17	4.34	6.14
MeOClO$_3$]/M	8.00	8.00	8.00		
10^3[MeONa]/M	7.80	11.70	19.50		
10^3k_1/s^{-1}	6.00	8.34	13.3		

[a] With [MeOClO$_3$] = 0.003 80M, solvent contained 4% (by volume) benzene and with [MeOClO$_3$] = 0.008 00M, solvent contained 2% (by volume) benzene. [b] In a more detailed study of the methanolysis, a value of 0.68 × 10^{-3} s^{-1} was obtained.[22]

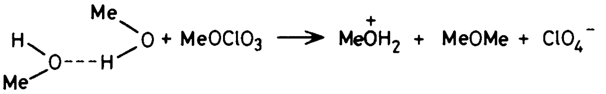
with sodium methoxide concentration and the increases corresponded to a superimposed second-order component to the solvolysis rate law (3) where k_2 is 0.67 l mol^{-1} s^{-1}.

$$-\mathrm{d}[\mathrm{MeOClO_3}]/\mathrm{d}t = k_2[\mathrm{MeOClO_3}][\mathrm{NaOMe}] \quad (3)$$

Discussion

The observation for methyl perchlorate solvolysis in hydroxylic solvents [22,23] of a kinetic pattern more consistent with a classical S_N2 mechanism than with either an S_N1 or a S_N2C^+ mechanism is supported by the present observation (Table 5) of a pronounced second-order reaction with added methoxide ion. Since bimolecular reactions dominate in hydroxylic solvents of relatively high ionizing power, they certainly would be expected to operate for reactions with moderate concentrations of hydroxylic addenda in inert solvents of low polarity, such as benzene. Indeed, if ionization of methyl perchlorate in benzene was to occur, one would expect to observe Friedel–Crafts alkylation, leading to toluene. Methyl perchlorate is inert towards solvent benzene [24] over extended periods of time and even addition of 0.45M-phenol, an aromatic compound very susceptible to electrophilic attack, did not lead to any detectable reaction over a period of 40 days.

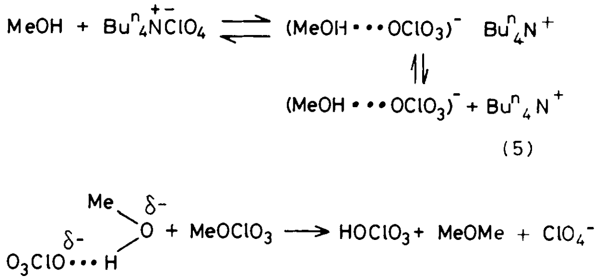
The order in methanol for the region of methanol concentration within which the two studies overlap (0.07—0.50M) is slightly less for reaction with methyl perchlorate than for reaction with triphenylmethyl chloride. For triphenylmethyl chloride, the order of somewhat over 2 was explained as being due to the cumulative effect of one methanol molecule acting as a nucleophile, one or more methanol molecules assisting the departure of the chloride ion, and a favourable influence of increased solvent polarity upon a reaction with which charges are produced.[13] While it is well established that, even in relatively polar solvents such as nitromethane or nitrobenzene, heterolytic development of halide ion can be assisted by specific solvation by methanol molecules,[25,26] such a process would not be expected to be as advantageous for perchlorate-ion development. The perchlorate ion can effectively disperse the developing charge internally and, in addition, it is an extremely lipophilic anion.[27] It has even been suggested that perchlorate ion is better solvated by dipolar aprotic solvents than by water.[28] Consistent with a reduced importance for electrophilic assistance is the observed absence of autocatalysis by the powerful acid, perchloric acid, which is produced during the methanolysis. For methanolysis of methyl perchlorate, an alternative involvement of additional methanol molecules by general-base catalysis, involving attack by a hydrogen-bonded polymer, would afford an effective way of dispersing the developing *positive* charge [reaction (4)]. The resultant stabilization of the transition state may, especially for substrates with leaving groups capable of dispersing negative charge other than through solvation, be greater than when additional methanol molecules are used to solvate the developing anion.



(4)

Added nitromethane, a relatively inert polar addendum, accelerates the reaction, consistent with the influence upon the rate-determining step to be expected for a reaction producing charged species from neutral reactants. However, addition of phenol, also considerably more polar than benzene, leads to appreciable decreases in rate, in contrast to the large increases observed when phenol was added to the methanolysis of triphenylmethyl chloride.[11,13] In addition to general polarity considerations, it would appear that addition of phenol to methanolyses in benzene leads to two opposing factors: an accelerative effect due to electrophilic assistance to removal of an anion from the substrate and a decelerative effect due to deactivation of methanol by mixed hydrogen bonding between the more acidic hydrogen of phenol and the more basic oxygen of methanol, such hydrogen bonding has been documented for interaction in carbon tetrachloride.[29a] It is reasonable, for reasons outlined above, that chloride-ion removal will be more sensitive towards electrophilic assistance than perchlorate-ion removal. Interpretations of previous studies in benzene appear to have considerably underemphasized the important interactions which are frequently to be expected between multiple addenda in low polarity solvents, interactions which will be present prior to involvement of the substrate or intermediates derived from the substrate.

Although symmetry prevents the operation of a Winstein special salt effect when tetra-n-butylammonium perchlorate (TNBAP) is added to the methanolysis of methyl perchlorate, a very pronounced catalysis of the methanolysis is observed and equation (2), with a half-order dependence on added TNBAP concentration, is accurately followed. This assistance to the methanolysis can be formulated in a parallel manner to the assistance derived from involvement of a second methanol molecule, but now involving general-base catalysis by perchlorate ion [reaction (5)].[29b] While perchlorate is generally considered to be very weak as either a base or a nucleophile, this is based on its behaviour in more polar solvents and, for example, the H(ClO$_4$)$_2^-$ ion has been observed in dichloromethane [30] and examples of nucleophilic [31–33] or basic [32] intervention by perchlorate ion are well documented.



Reaction (5) will lead to the observed half-order dependence upon TNBAP concentration provided that the equal concentrations of free ions produced *via* the interaction of TNBAP ion pairs with methanol molecules are relatively low. Since at the transition state of the rate-determining step a methanol

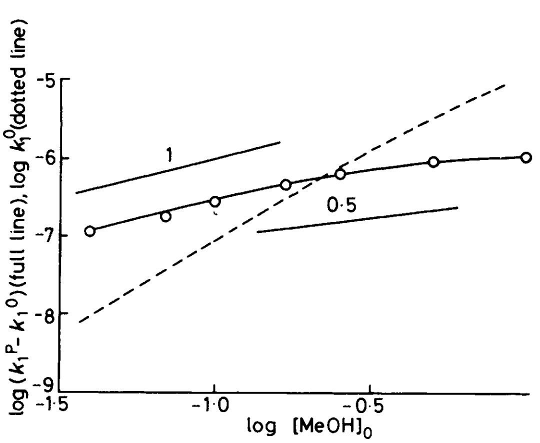


Figure 2. Effect of methanol concentration on the rate of the TNBAP catalysed methanolysis of methyl perchlorate in benzene at 25.0 °C. The continuous curve represents the plot of the excess rate at 0.0005M-TNBAP concentration *versus* the logarithm of the methanol concentration. The broken line shows the effect of methanol concentration on the rate of methanolysis in the absence of the catalyst (salt-free rate). The straight lines show theoretical slopes for kinetic orders of 0.5 and 1 with respect to methanol

molecule is replaced by a perchlorate ion, one would expect a reduced order in methanol. Indeed, in the absence of superimposed polarity effects, reaction (5) would predict a fall in the value for the order in methanol to one-half. The experiments required to test this hypothesis are reported in Table 4. From the k_1^p values (specific rate in presence of catalyst), one must deduct the k_1^0 values in the absence of TNBAP (the k_1 values of Table 1); some of the salt-free values were obtained by interpolation. In Figure 2, logarithmic plots of log $(k_1^p - k_1^0)$ and of log k_1^0 against methanol concentration are presented. It can be seen that the order in methanol is indeed considerably reduced for the perchlorate-ion catalysed component to the reaction and it is of value not considerably higher than one half.

That the perchlorate-ion catalysis does indeed involve a specific involvement, rather than a very powerful generalized salt effect,[34] is strongly indicated by a considerably reduced effect upon the identical charge type reaction of methyl perchlorate with *NN*-dimethylaniline in benzene.[6] For this system, involvement of a tertiary amine prevents the operation of a general-base-catalysis mechanism.

It is surprising to find that the *b* value of 163 $l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ is virtually identical to values which can be calculated from the effect of TNBAP upon the methanolysis of triphenylmethyl chloride.[13] Neglecting catalysis by adventitious acid, one can arrive at a value of 134 ± 14 $l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ at up to 2×10^{-4}M-TNBAP concentration, falling to a value of 94 $l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ at 2×10^{-3}M. Assuming acid and TNBAP catalyses are additive,[13] the corresponding values are 199 ± 21 $l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$ falling to 139 $l^{\frac{1}{2}}$ mol$^{-\frac{1}{2}}$. Since methyl perchlorate cannot be subject to the same type of catalysis as that previously proposed for triphenylmethyl chloride, the question arises as to whether triphenylmethyl chloride is undergoing an S_N2-type reaction [19] which is susceptible to general-base catalysis. However, other features, principally the rate *depressions* caused by relatively low concentrations of tetra-n-butylammonium chloride (TNBAC),[13,16] argue against such a mechanism. If the reaction was S_N2 in character, chloride-containing salt would be expected to be an even more effective general base than perchlorate-containing salt.

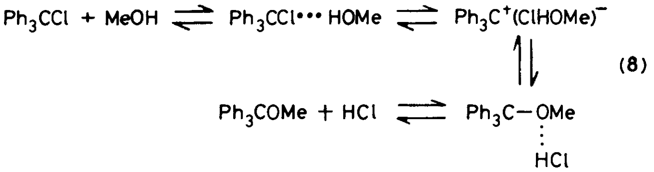
The mechanism of the TNBAC retardations has been difficult to explain.[15-18] Interaction of either Cl^- or $Bu^n_4\overset{+}{N}Cl^-$ with a $Ph_3C^+Cl^-$ ion pair would eventually be expected to produce along the reaction co-ordinate a new $Ph_3C^+Cl^-$ ion pair and interactions such as (6) [16] cannot be the source of the retardation. The S_N2C^+ scheme, with attack upon an ion pair, (7), proposed by Swain and Pegues,[15] does not allow for a TNBAC retardation, a retardation which was subsequently confirmed.[16]

$$Ph_3C^+Cl^- + Bu^n_4N^+Cl^- \longrightarrow Ph_3CCl + Bu^n_4\overset{+}{N}Cl^- \qquad (6)$$

$$Ph_3CCl \rightleftharpoons Ph_3C^+Cl^- \xrightarrow[\text{slow}]{MeOH} Ph_3COMe + HCl \qquad (7)$$

Swain and Pegues [15] considered the absence of an isotope effect when either methanol or [^{2}H]methanol in low concentration were reacted with triphenylmethyl chloride in benzene to indicate nucleophilic rather than electrophilic interaction of the one methanol molecule involved. However, it has since been shown that, in carbon tetrachloride, methanol and [^{2}H]methanol have virtually identical equilibrium constants and bond strengths for complexing with a variety of bases [35] and it would appear that this isotope study does not allow a choice to be made between a nucleophilic or an electrophilic role for the one methanol molecule involved in the rate law at low concentrations.

The observation of phenolysis with retention of configuration in several nucleophilic substitution reactions carried out in phenol–benzene mixtures [36,37] is probably best explained in terms of initial electrophilic assistance to removal of the leaving group followed by frontside collapse of the carbenium ion with the oxygen of the phenol molecule, now constituting one of the nucleophilic centres within an ambident anion. A parallel scheme for the methanolysis of triphenylmethyl chloride would be as in reaction (8). The basic assumptions are that the *unassisted* ionization is followed almost invariably by internal return to reactant and methanol can serve a dual role, first rendering electrophilic assistance to carbenum ion formation and then, within the ambident anion formed, attack at oxygen can compete with attack at chlorine. External attack by a second methanol molecule on $Ph_3C^+(ClHOMe)^-$ is in principle possible but cannot apply at low concentrations, since the order in methanol is unity. Also, the observation that addition of a 54-fold excess of water does not change the *methanolysis* rate [15] argues against such involvement, since a parallel attack of methanol on $Ph_3C^+(ClHOH)^-$ or of water on $Ph_3C^+(ClHOMe)^-$ is, apparently, not operative.


(8)

$$\begin{array}{ccccc} Ph_3CCl + MeOH & \rightleftharpoons & Ph_3CCl\cdots HOMe & \rightleftharpoons & Ph_3C^+(ClHOMe)^- \\ & & & & \upharpoonleft\downharpoonright \\ & & Ph_3COMe + HCl & \rightleftharpoons & \begin{array}{c} Ph_3C{-}OMe \\ \vdots \\ HCl \end{array} \end{array} \qquad (8)$$

When tetra-n-butylammonium salts are added, one must consider the interaction of these salts with the methanol [reaction (9)]. When the X^- of reaction (9) is perchlorate ion an accelerative effect of one-half order in added salt is observed [13,17] and this can be explained, as in the present

Table 6. Illustrations of methanolysis of methyl perchlorate in benzene

(A) [$MeOClO_3$] 0.0400M, [MeOH] 0.100M

t/min	1 320	2 610	5 730	7 110	8 520
% Reaction	0.7	1.3	3.2	4.0	4.6
10^7k_2/l mol^{-1} s^{-1}	8.81	8.07	9.50	9.53	9.29

t/min	9 720	11 280	12 660	13 980
% Reaction	5.3	5.9	6.8	7.5
10^7k_2/l mol^{-1} s^{-1}	9.33	9.09	9.31	9.45

(B) [$MeOClO_3$] 0.0400M, [MeOH] 0.100M, [PhOH] 0.224M

t/min	6 975	8 700	10 740	12 180	18 600	25 530
% Reaction	1.6	2.1	2.5	3.0	4.4	6.2
10^7k_2/l mol^{-1} s^{-1}	3.88	4.03	3.97	4.12	4.08	4.23

(C) [$MeOClO_3$] 0.0400M, [MeOH] 0.100M, [TNBAP] 0.000 25M

t/min	660	1 380	2 070	3 480	4 950	6 390
% Reaction	1.1	2.0	2.7	4.0	5.0	6.1
10^7k_2/l mol^{-1} s^{-1}	28.1	23.9	21.6	19.5	17.2	16.5

Initial k_2 value (by extrapolation) of 34.2×10^{-7} l mol^{-1} s^{-1}.

methyl perchlorate study, by the involvement of a low concentration of $(O_3ClO \cdots HOMe)^-$ free ion. For the triphenylmethyl chloride system, the interaction is essentially an example of a modified Winstein special salt effect [18,38] [reaction (10)]. The new ion pair will have no tendency to

$$Bu^n{}_4\overset{+}{N}X^- + MeOH \rightleftharpoons Bu^n{}_4\overset{+}{N}(XHOMe)^- \rightleftharpoons Bu^n{}_4\overset{+}{N} + (XHOMe)^- \qquad (9)$$

$$Ph_3C^+Y^- + (O_3ClOHOMe)^- \rightleftharpoons Ph_3C^+(O_3ClOHOMe)^- + Y^- \qquad (10)$$

$Y^- = Cl^-$ or $(ClHOMe)^-$

collapse at perchlorate (triphenylmethyl perchlorate is an ionic compound, even in the solid state [39]) and the circumvention of internal return will lead to an accelerated methanolysis. The observation of a cancellation of the TNBAP catalysis by the simultaneous addition of the chloride-ion containing TNBAC parallels observations made upon other systems,[18,40] where the Winstein special salt effect has been found to be subject to ' induced common ion rate depression ' [reaction (11)].

$$\begin{array}{l} Ph_3C^+(O_3ClOHOMe)^- + Bu^n{}_4\overset{+}{N}Y^- \\ \qquad\qquad \upharpoonleft\downharpoonright \\ Ph_3C^+Y^- + Bu^n{}_4\overset{+}{N}(O_3ClOHOMe)^- \end{array} \qquad (11)$$

$Y^- = Cl^-$ or $(ClHOMe)^-$

An important consequence of proposing an initially electrophilic interaction of the methanol is that it allows a simple explanation of the previously puzzling retardation of the methanolysis by added TNBAC. When the X^- of reaction (9) is chloride ion, interactions of $(ClHOMe)^-$, either as the free ion or paired with a tetra-n-butylammonium ion, with $Ph_3C^+(ClHOMe)^-$ will be symmetrical. However, the $Bu^n{}_4\overset{+}{N}Cl^-$ ion pairs within the equilibrium will undergo an exchange reaction with the $Ph_3C^+(ClHOMe)^-$ intermediates, to give $Ph_3C^+Cl^-$ ion pairs; these will then collapse to substrate. In this way, a new external route for return to substrate, closely related to the induced common ion rate depression mentioned above, is superimposed upon the internal collapse with the chloride of $Ph_3C^+(ClHOMe)^-$, and a retardation of the methanolysis is observed [reaction (12)]. This mechanism for the retardation of the methanolysis

$$\begin{array}{llll} Ph_3C^+(ClHOMe)^- + Bu^n{}_4\overset{+}{N}Cl^- & \rightleftharpoons & Ph_3C^+Cl^- + Bu^n{}_4\overset{+}{N}(ClHOMe)^- & (12) \\ & & \quad\downarrow & \\ & & Ph_3CCl & \end{array}$$

also explains why added methanol considerably accelerates the exchange reaction between triphenylmethyl chloride and tetra-n-butylammonium radiochloride.[7] A secondary factor, which will lead to rate depression, is that the complexing of methanol molecules with TNBAC ion pairs [reaction (9; X = Cl)] will reduce the concentration of methanol molecules available for electrophilic interaction with the substrate [reaction (8)].

Experimental

Materials.—Spectrograde benzene was dried over $CaCl_2$ for one week and fractionally distilled. The middle fraction was stored over Linde 4A molecular sieves and passed through a column of molecular sieve powder immediately before use; no water was detected by Karl Fischer titration. Phenol was dried over P_2O_5 for several days and then recrystallized from purified benzene. A benzene solution of the recrystallized product was passed through a 12-inch column of Linde 4A molecular sieves prior to use and the concentration was then determined by bromination of a portion and back-titration of excess of bromine.[41] The preparation of a benzene solution of methyl perchlorate [6] and the purification of tetra-n-butylammonium perchlorate [42] and nitromethane [43] have previously been described.

A 0.4M solution of MeO_i–ClO_3 in benzene gave an i.r. spectrum including a doublet at 1 230 and 1 260 cm^{-1}, assigned to Cl–O_i asymmetric stretching and previously observed for (C_6-C_8) n-alkyl perchlorates.[44] The ^1H n.m.r. spectrum of a 0.2M solution showed only one signal (CH_3OClO_3; δ 3.13) in the region where methyl signals might reasonably be expected. In particular, no signal was observed in the region of δ 2.14, confirming that toluene is not a product of the reaction of methyl iodide with silver perchlorate in benzene.[24]

Kinetics.—All glassware was purged before use with air which had been dried by passage through a tower packed with granular molecular sieves. Standard solutions of the reagents and the solvent were equilibrated at 25.00 ± 0.05 °C before mixing. The rate of acid formation was followed by quenching 5 ml portions of the reaction mixture in 100 ml of a saturated solution of lithium chloride in acetone, followed by the titration of the perchloric acid (which had been produced prior to quenching) against a standardized solution of sodium methoxide in methanol to a Lacmoid (Resorcinol Blue) endpoint.

Integrated second-order rate coefficients, calculated according to $d[HClO_4]/dt = k_2[MeOClO_3][MeOH]$, were essentially constant throughout each run for the methanolysis and for methanolyses in the presence of added phenol and nitromethane; multiplying average values by the initial methanol concentration gave the initial specific rates which are reported in Tables 1 and 2. In the presence of TNBAP, the integrated second-order rate coefficients fell in value as reaction progressed, presumably because of deactivation of perchlorate ion by the perchloric acid produced[30,32] $[HClO_4 + ClO_4^- \rightleftharpoons H(ClO_4)_2^-]$, and initial values were obtained by extrapolation (Tables 3 and 4).

For the runs containing sodium methoxide, after quenching, a measured excess of a standardized solution of HCl in methanol was added, followed by back-titration with NaOMe in MeOH.

Three illustrative runs are given in Table 6.

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