The N-phenylthiocarbamyl derivative was prepared in 82% yield in Skellysolve B: mp 103–109°; recrystallized from Skellysolve B-acetone, mp 114–115°.

Anal. Calcd for $C_{12}H_{15}N_2S$: C, 65.71; H, 6.89. Found: C, 65.72; H, 7.18.

2-Azido-3-iodo-2-methylpentane (55) was prepared from 2-methyl-2-pentene in 60% yield after purification on an alumina column: nmr (CCl_4) τ 4.11 (m, 1, C*H*–I), 8.20 (m, 2), 8.48 (s, 3), 8.54 (s, 3), and 8.93 (t broad, 3).

Anal. Calcd for $C_6H_{12}IN_3$: C, 28.47; H, 4.78. Found: C, 28.69; H, 4.89.

3-Ethyl-2,2-dimethylaziridine (57). LAH reduction of 10.8 g of **55** gave 2.50 g of a volatile liquid; nmr (CCl_4) τ 9.30 (s broad, 1, $W_{1/2}$ = 6 Hz, exchangeable N–H), 8.40–9.15 (m).

The N-phenylthiocarbamyl derivative was prepared in 88% yield in Skellysolve B: mp 87–90°; recrystallized from Skellysolve B-acetone, mp 90–91°.

Anal. Calcd for $C_{13}H_{18}N_2S$: C, 66.62; H, 7.74. Found: C, 66.67; H, 7.65.

The N-p-nitrobenzoyl derivative melted at 55.5–57.5° after recrystallization from pentane.

Anal. Calcd for $C_{13}H_{16}O_2N$: C, 62.89; H, 6.50. Found: C, 62.92; H, 6.52.

A higher melting product was obtained from the mother liquors of the N-p-nitrobenzoyl derivative recrystallizations. The side product was characterized as N-p-nitrobenzoyl-3-amino-2-methyl-pentan-2-ol: mp 132–134°; mp 135–137° after recrystallization from Skellysolve F-ethyl acetate; nmr $(CDCl_3$ and a trace of DMSO-d_6) τ 1.80 (A_2B_2 pattern, 4), 2.17 (d broad, 1, J = 10 Hz), 6.08 (t of doublets, 1, J = 10 Hz; J = 3.5 Hz), 2.3 (m, 2), 8.78 (d, 6), and 9.08 (t broad, 3, J = 7 Hz).

Anal. Calcd for $C_{13}H_{18}O_4N_2$: C, 58.63; H, 6.81. Found: C, 58.65; H, 6.77.

2,2,3,3-Tetramethylaziridine. LAH reduction of 10.0 g of 2-azido-3-iodo-2,3-dimethylbutane[13] gave, after distillation of the ether at *ca.* 20 mm, 2.20 g of a volatile liquid, the ir spectrum of which was identical with that reported;[2] nmr (CCl_4) τ 8.80 (s) and 2% of tetramethylethylene by integration of the 8.39 singlet.

The N-p-nitrobenzoyl derivative (100%) melted at 135–139°: mp 140–141° after recrystallization from Skellysolve B-trace of benzene; ir (KBr) 1640 cm^{-1}.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 62.89; H, 6.50. Found: C, 63.04; H, 6.70.

Acylation Mechanisms in Aprotic Solvents. I. Methanolysis of p-Nitrobenzoyl Chloride in Acetonitrile[1]

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Abstract: Contrary to previous proposals, the third-order kinetic term frequently observed for alcoholyses of acyl halides in aprotic solvents does not result from a push–pull mechanism. The methanolysis of p-nitrobenzoyl chloride (PNBC) in acetonitrile obeys the kinetic formulation: $d[HCl]/dt = k_2[PNBC][MeOH] + k_3[PNBC][MeOH]^2$. The reaction is not catalyzed by addition of phenol, a more electrophilic but less nucleophilic species than methanol, and an alternative mechanism is proposed in which, for over-all reaction, a first-formed tetrahedral intermediate is deprotonated by either a solvent molecule (second-order kinetics) or a second methanol molecule (third-order kinetics) to give a new tetrahedral intermediate which collapses to products. Consistent with this formulation, addition of chloride ion (a strong base in acetonitrile) leads to a tremendous acceleration and, for a given methanol concentration, this has the formulation: $d[HCl]/dt = k_3'[PNBC][MeOH][Cl^-]$. With increase in [MeOH], there is an appreciable decrease in k_3', consistent with a reduction in chloride ion basicity due to specific solvation. The claim by Briody and Satchell to have excluded the possibility of a tetrahedral intermediate mechanism for acetonitrile reactions of chloroacyl chlorides with phenols, and to have established a synchronous SN2 type mechanism, is questioned and an alternative explanation of their kinetic data in terms of conventional ionization and tetrahedral intermediate mechanisms is presented.

Several studies of the ethanolysis of acyl chlorides in aprotic solvents have led to third-order kinetics, first order in acyl halide and second order in ethanol.[2–4] The apparent involvement of two alcohol molecules has usually been explained[4,5] in terms of a push–pull mechanism of the type postulated by Swain for substitution reactions at a saturated carbon.[6]

Although alcohol molecules can serve as electrophilic as well as nucleophilic reagents,[7] it must be borne in mind that the mechanism for direct nucleophilic attack upon substrate molecules is considered to have different characteristics for attack at a saturated and at a carbonyl carbon. An extension, merely on the basis of kinetic similarities, of theories applied to one class of substitutions to those of the other type must be regarded as, at best, a dubious procedure.

Renewed interest in these reactions arose following studies in our laboratories of the reactions between alkyl chloroformates and silver nitrate in acetonitrile,[8,9] the

(1) (a) A preliminary communication of a portion of these results has appeared previously: D. N. Kevill and F. D. Foss, *Tetrahedron Letters*, 2837 (1967). (b) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) A. A. Ashdown, *J. Amer. Chem. Soc.*, **52**, 269 (1930).

(3) R. F. Hudson and B. Saville, *J. Chem. Soc.*, 4121 (1955).

(4) W. R. Gilkerson, *J. Phys. Chem.*, **60**, 1142 (1956).

(5) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 334.

(6) C. G. Swain, *J. Amer. Chem. Soc.*, **70**, 1119 (1948).

(7) Y. Pocker, *J. Chem. Soc.*, 1179 (1959).

(8) D. N. Kevill and G. H. Johnson, *J. Amer. Chem. Soc.*, **87**, 928 (1965).

(9) D. N. Kevill and G. H. Johnson, *Chem. Commun.*, 235 (1966).

Table I. Experimental Second-Order Rate Coefficients for Reaction of 0.16 M Methanol with p-Nitrobenzoyl Chloride in Acetonitrile at 25.0°

[PNBC], M	0.02	0.04	0.04	0.16
$10^4k_2'$, l. mol^{-1} sec^{-1}	0.92 ± 0.01	0.90 ± 0.01	0.93 ± 0.03	0.95 ± 0.03

isolated substitution product being the alkyl nitrate.[10]

$$\underset{\underset{O}{\|}}{ROCCl} + AgNO_3 \longrightarrow RONO_2 + CO_2 + AgCl$$
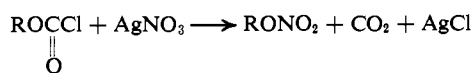
It was found that the reaction proceeded either with a rate-limiting nucleophilic attack by the nitrate ion or with a rate-determining electrophilic assistance by the silver ion but not with both factors simultaneously. This was in contrast to previous studies in acetonitrile in which the substrates were alkyl halides and in which simultaneous nucleophilic and electrophilic assistance was observed in reactions with silver nitrate.[11,12] Since at least one reaction which possessed push–pull character when applied to an alkyl halide did not when applied to an acyl halide, we considered the application of push–pull theory to the alcoholyses of acyl halides, upon the basis of studies with alkyl halides, to be extremely suspect.

The system chosen for study was the methanolysis of p-nitrobenzoyl chloride in acetonitrile. Acetonitrile

$$p\text{-}NO_2C_6H_4COCl + MeOH \longrightarrow p\text{-}NO_2C_6H_4COOMe + HCl$$
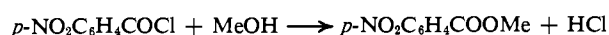
was chosen since good purification techniques are available,[13] and p-nitrobenzoyl chloride was selected because it can readily be purified by recrystallization. The extent of reaction at any given time can be conveniently determined by monitoring the production of hydrogen chloride.

Results and Discussion

Reaction with Methanol. The methanolysis of p-nitrobenzoyl chloride (PNBC) in acetonitrile was studied at several temperatures and over a wide range of methanol concentration. At each temperature, the kinetics was found to be represented by the expression

$$d[HCl]/dt = k_2[PNBC][MeOH] + k_3[PNBC][MeOH]^2$$

For reaction with p-nitrobenzoyl chloride concentrations of up to 0.16 M, the kinetics could be very well described, over an appreciable extent of reaction, in terms of experimental second-order rate coefficients.

$$d[HCl]/dt = k_2'[PNBC][MeOH]$$

This was due to the approximation toward second-order kinetics at low methanol concentrations coupled with an insensitivity toward the order in methanol when its initial concentration was in appreciable excess over that of p-nitrobenzoyl chloride. The experimental second-order rate coefficients are reported in Tables I and II.

From the data presented in Table II, it is possible at each temperature to calculate the second- and third-order rate coefficients for the two terms contributing toward the over-all rate expression and, in turn, the Arrhenius parameters can be obtained for each of the

coefficients. Plots of k_2' against [MeOH] are linear, with intercept k_2 and slope k_3, for up to about 1 M methanol concentration. At higher methanol concentrations, and especially at the lower temperatures, there is a tendency toward a gradual steepening of the slope. This is not surprising because a region in which the reaction should be considered as a solvolysis in a mixed solvent of varying composition, rather than as a methanolysis in acetonitrile as solvent, is being approached. Indeed, the observation of a rather extensive linear range is probably possible only because the dielectric constants of acetonitrile, methanol, and acetonitrile–methanol mixtures are quite similar[14] (see Table III).

Table II. Experimental Second-Order Rate Coefficients for Reaction of 0.04 M p-Nitrobenzoyl Chloride with Methanol in Acetonitrile at Various Temperatures.

[MeOH], M	$10^4k_2'$, l. mol^{-1} sec^{-1} [a]			
	0°	25.0°	35.0°	45.0°
0.01	0.065	0.51		1.37
0.02	0.085	0.49	1.04	1.44
0.04	0.085	0.55	1.11	1.68
0.08	0.107	0.63	1.20	2.07
0.16	0.163	0.93	1.63	2.57
0.32	0.315	1.48	2.24	3.87
0.64	0.530	2.55		7.29
0.96	0.748	3.91		9.41
1.02	0.854			
1.28	1.08	5.19	7.48	12.15
1.60	1.41	6.17	9.45	14.68

[a] Standard deviations, calculated for each run, were in all instances less than ±5% of the reported values.

Table III. Second- and Third-Order Rate Coefficients at Various Temperatures

	Temp, °C			
	0.0	25.0	35.0	45.0
10^4k_2, l. mol^{-1} sec^{-1} [a]	0.060	0.41	0.80	1.27
10^4k_3, l.^{2} mol^{-2} sec^{-1} [b]	0.768	3.31	5.40	8.53

[a] $k_2 = A_2e^{-E_2/RT}$, log $A_2 = 4.38 ± 0.62$, $E_2 = 12.07 ± 0.83$ kcal/mol. [b] $k_3 = A_3e^{-E_3/RT}$, log $A_3 = 3.36 ± 0.09$, $E_3 = 9.34 ± 0.11$ kcal/mol.

Reaction with Phenol. The reaction with weakly nucleophilic phenol substituted for methanol is very slow and appreciably faster than the background rate of acid production only for fairly large concentrations of phenol. The results are summarized in Table IV.

Table IV. First- and Second-Order Rate Coefficients for Reaction of 0.04 M p-Nitrobenzoyl Chloride with Phenol in Acetonitrile at 25.0°

	[PhOH], M		
	0.00	0.64	1.13
$10^8k_1''$ [a]	3.7 ± 0.7	23 ± 6	32 ± 7
$10^8k_2''$ [b,c]		30 ± 10	25 ± 7

[a] $d[HCl]/dt = k_1''[PNBC]$. [b] $d[HCl]/dt = k_2''[PNBC][PhOH]$. [c] Corrected for background reaction.

(10) R. Boschan, *J. Amer. Chem. Soc.*, **81**, 3341 (1959).
(11) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *ibid.*, **82**, 704 (1960).
(12) Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965).
(13) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).
(14) E. A. S. Cavell, H. G. Jerrard, B. A. W. Simmonds, and J. A. Speed, *J. Phys. Chem.*, **69**, 3657 (1965).

Table V. Experimental Second-Order Rate Coefficients for Methanolysis of 0.04 M p-Nitrobenzoyl Chloride in Acetonitrile at 25.0° in the Presence of Phenol

[MeOH], M	0.02	0.02	0.02	0.02	0.02	0.02	0.32	0.32	0.32
[PhOH], M	0.00	0.014	0.028	0.056	0.16	0.64	0.00	0.32	0.64
$10^4 k_2'$, l. mol^{-1} sec^{-1} [a,b]	0.49	0.59	0.61	0.63	0.59	0.62	1.48	1.33	1.59

[a] $d[HCl]/dt = k_2'[PNBC][MeOH]$.   [b] Standard deviations for any given run less than ±8%.

**Reaction with Mixtures of Methanol and Phenol.** Since methanol is efficient as a nucleophile and phenol is efficient as an electrophile, a push–pull mechanism would be favored by use of a mixture of the two reagents. Accordingly, if phenol and methanol are both present, the favored push–pull reaction path would be
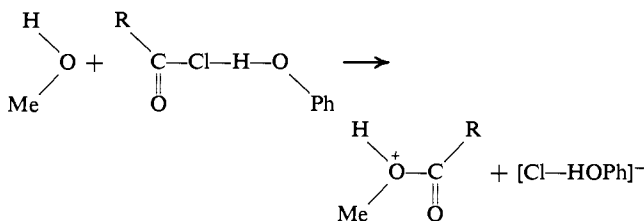
and a new third-order term would be added to the rate expression—a term of first order in each of the three reactants.[5]

Table V summarizes the reaction rate studies carried out with constant concentrations of p-nitrobenzoyl chloride and methanol and with varying concentrations of phenol.

The absence of any perturbation, even with as much as a 32-fold excess of phenol over methanol, shows that phenol can be considered as an inert additive and the methanolysis proceeds by the same reaction paths as those observed in its absence. Since the third-order term for the methanolysis cannot involve electrophilic assistance by a second methanol molecule to the nucleophilic methanolysis, a new mechanism must be postulated for this term. We believe that the over-all kinetic pattern can be very well explained in terms of a single mechanism which involves attack by a nucleophilic methanol molecule to form a tetrahedral intermediate (I). This intermediate normally reverts to reactants unless deprotonation occurs to give a new tetrahedral intermediate (II) which normally proceeds to products.
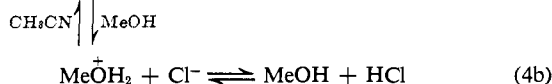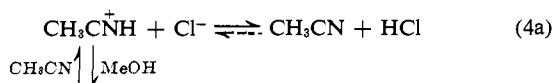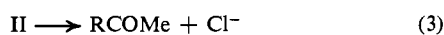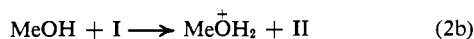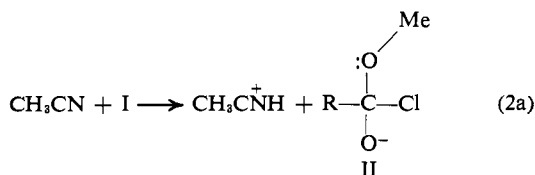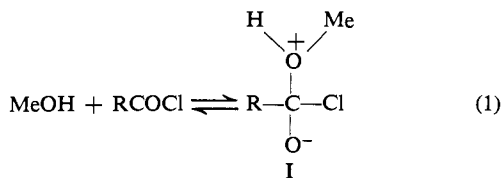
In the absence of a hydroxylic solvent, the fast proton transfer reactions which would convert I to its uncharged tautomer do not occur and regeneration of the carbonyl group from I will lead preferentially to loss of methanol rather than chloride. Deprotonation of I, an essential step for over-all reaction, can proceed with attack either by the weakly basic solvent molecules (second-order kinetics) or by the more strongly basic, but less plentiful, methanol molecules (third-order kinetic). The new intermediate, II, on regeneration of the carbonyl group will lose chloride in preference to methoxide and ester formation will result. In this scheme for the third-order term, both methanol molecules are acting as nucleophiles (bases) and accordingly no catalysis would be expected on adding the weakly nucleophilic (basic) phenol—in accord with observations. In principle, a test of the above mechanism is quite easy. Since both acetonitrile and methanol are quite weak bases, addition of a fairly strong base should cause a tremendous acceleration due to the introduction of a facile deprotonation step. Unfortunately, in the general case, the investigation would be complicated by the facile intervention which will also occur between the acyl chloride and any added base.

$$RCOCl + :B^- \rightleftharpoons RCOB + Cl^-$$

There is however one base, which is quite strong in acetonitrile due to the absence of hydrogen-bonded solvation, which can be added so as to provide a simple test of the proposed mechanism. The ready interaction by the chloride ion at the acyl carbon will merely regenerate substrate by a symmetrical exchange and its intervention in the deprotonation step of the mechanism can be studied.

Methanolysis in the Presence of Added Chloride Ion. Addition of tetraethylammonium chloride to the reaction of 0.04 M p-nitrobenzoyl chloride with 0.02 M methanol at 0.0° caused a tremendous acceleration and appreciable, but reduced, accelerations were observed for similar additions but with use of higher methanol concentrations (Table VI).

For a given methanol concentration, addition of tetraethylammonium chloride leads to a linear increase in rate due to introduction of a new deprotonation step.
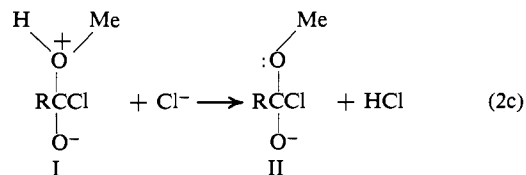
A change from 0.02 to 1.60 M methanol reduces the catalytic effect and there is an approximately 70-fold reduction in the value for the k_3' third-order rate coefficient. A detailed study of the influence of methanol concentration upon the chloride ion catalysis was undertaken (Table VII).

Table VI. Initial Second- and Third-Order Rate Coefficients for the Tetraethylammonium Chloride Catalyzed Reaction of Methanol with 0.04 M p-Nitrobenzoyl Chloride in Acetonitrile at 0.0°

i. With 0.0200 M Methanol

	[NEt₄Cl], M				
	0.000	0.0135	0.0190	0.0270	0.0390
$10^3k_2'$, l. mol⁻¹ sec⁻¹ [a]	0.009	14	18	25	36
k_3', l.² mol⁻² sec⁻¹ [b]		1.04	0.95	0.93	0.92

	[NEt₄Cl], M			
	0.0520	0.0650	0.135	0.162
$10^3k_2'$, l. mol⁻¹ sec⁻¹	53	67	118	146
k_3', l.² mol⁻² sec⁻¹	1.02	1.03	0.87	0.90

ii. With 0.160 M Methanol

	[NEt₄Cl], M					
	0.000	0.0095	0.0193	0.0380	0.0760	0.152
$10^3k_2'$, l. mol⁻¹ sec⁻¹	0.0163	1.7	4.7	8.0	14.9	25.1
k_3', l.² mol⁻² sec⁻¹		0.179	0.244	0.211	0.196	0.165

iii. With 1.60 M Methanol

	[NEt₄Cl], M				
	0.000	0.0190	0.0380	0.0760	0.152
$10^3k_2'$, l. mol⁻¹ sec⁻¹	0.141	0.476	0.67	1.20	2.04
k_3', l.² mol⁻² sec⁻¹ [c]		0.0176	0.0140	0.0140	0.0125

[a] $d[HCl]/dt = k_2'[PNBC][MeOH]$. [b] $d[HCl]/dt = k_3'[PNBC][MeOH][NEt_4Cl]$. [c] For reaction with 1.60 M methanol, the reaction rates used for calculating third-order rate coefficients were corrected for the appreciable methanolysis proceeding without chloride ion catalysis.

Table VII. Initial Second- and Third-Order Rate Coefficients for the Reaction, in Acetonitrile at 0.0°, of 0.04 M p-Nitrobenzoyl Chloride with Methanol in the Presence of 0.0190 M Tetraethylammonium Chloride

	[MeOH], M					
	0.0096	0.0100ᵃ	0.0200	0.0400	0.0800	0.160
$10^3k_2'$, l. mol⁻¹ sec⁻¹	27.7	22.4ᵃ	18.0	13.0	8.1	4.7
$10^2k_3'$, l.² mol⁻² sec⁻¹ [b]	146	122	93	68	43	24

	[MeOH], M				
	0.320	0.640	0.960	1.28	1.60
$10^3k_2'$, l. mol⁻¹ sec⁻¹	2.7	1.40	0.71	0.64	0.48
$10^2k_3'$, l.² mol⁻² sec⁻¹ [b]	14.2	7.1	3.3	2.8	1.76

[a] [NEt₄Cl] = 0.0183 M. [b] For methanol concentrations of 0.64 M and above, calculated after correction of the over-all reaction rate for the rate of the methanolysis proceeding without chloride ion catalysis.

The sharp decrease in the third-order rate coefficients with increasing methanol concentration shows that an appreciable chloride ion catalysis would not be expected in methanol or methanol-rich solvents. The observations are consistent with the widely held view that small ions which readily engage in hydrogen bonding are relatively unsolvated and therefore reactive in dipolar aprotic solvents but quite tightly solvated, and therefore some 10^4 to 10^{10} times less reactive,[15] in hydroxylic solvents such as methanol. Presumably, even a relatively small amount of methanol in acetonitrile is sufficient to

(15) (a) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, J. Amer. Chem. Soc., 90, 5049 (1968); (b) see also, however, P. Haberfield, L. Clayman, and J. S. Cooper, ibid., 91, 787 (1969).

lead to appreciable specific solvation. As one would

$$n\text{MeOH} + Cl^- \rightleftharpoons [(MeOH)_n\text{---}Cl]^-$$

expect,[15] the relative reductions observed for the rate coefficients are considerably greater than those observed for methanol additions to the symmetrical exchange reaction, in acetonitrile, of the larger radioiodide ions and n-butyl iodide, where 1 M methanol approximately halved the value of the second-order rate coefficient for the SN2 reaction.[16]

One feature of this hydrogen-bonded solvation is that concurrent with a decrease in the nucleophilicity (basicity) at the chloride ion there should be a corresponding increase in the nucleophilicity (basicity) at the methanolic oxygen and the decrease in rate due to solvation of the chloride ion may possibly be counterbalanced to some extent by a corresponding increase in the nucleophilicity of the methanolic oxygen of a solvation complex.

The catalytic action of the chloride ion is destroyed as reaction proceeds by a complexing with the developing hydrogen chloride to give the hydrogen dichloride anion

$$HCl + Cl^- \rightleftharpoons HCl_2^-$$
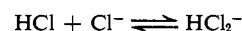
and the rate coefficients reported in Tables VI and VII are values obtained during the initial stages of reaction.

The involvement of the chloride ion in a specific role, and not just as an agent for introducing a powerful salt effect, was shown by adding tetraethylammonium perchlorate, which contains an extremely weakly basic anion. Reaction of 0.0400 M p-nitrobenzoyl chloride with 0.0200 M methanol at 25.0° had a second-order rate coefficient of 0.49 × 10⁻⁴ l. mol⁻¹ sec⁻¹ which increased to 0.61 × 10⁻⁴, 0.74 × 10⁻⁴, and 0.90 × 10⁻⁴ l. mol⁻¹ sec⁻¹ on addition of 0.0100, 0.0400, and 0.160 M tetraethylammonium perchlorate. The relative increases are four powers of ten lower in magnitude than those with corresponding concentrations of the chloride salt.

Methanolysis in Nitromethane. A brief study was carried out at 25.0° of the methanolysis of p-nitrobenzoyl chloride in nitromethane. The concentration range was limited by loss of hydrogen chloride during the runs carried out with methanol concentrations of 0.08 M and lower. This loss, which we believe to be physical, probably arises from a combination of longer reaction times coupled with a reduction in the specific solvation of the developing acid at the lower concentrations of methanol. The kinetics were accurately third order (Table VIII), first order in acyl chloride and

Table VIII. Third-Order Rate Coefficients for Methanolysis of 0.04 M p-Nitrobenzoyl Chloride in Nitromethane at 25.0°

	[MeOH], M					
	0.160	0.320	0.640	0.960	1.28	1.60
10^4k_3, l.² mol⁻² sec⁻¹ [a]	6.38	5.91	6.08	6.02	6.26	6.11

[a] Standard deviations, calculated for each run, were in all instances less than ±4% of the reported values.
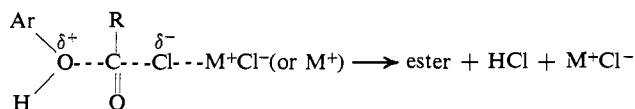
second order in methanol. However, this does not rule out a small second-order contribution which would be overwhelmed by the third-order contribution for our range of fairly high methanol concentrations.

(16) E. A. S. Cavell and J. A. Speed, J. Chem. Soc., 226 (1961).

Discussion of Formulation in Terms of a Tetrahedral Intermediate as Opposed to Synchronous Bond Making and Breaking. In keeping with current convention, we have formulated our reaction schemes in terms of the interconversion of tetrahedral intermediates. However, the results do not in themselves demand this particular formulation and attack by methanol monomers, by relatively small concentrations of methanol dimers in equilibrium with the monomer, or by relatively small concentrations of a chloride-ion–methanol-hydrogen-bonded complex in equilibrium with methanol and chloride ion, could also lead to the observed kinetics with the reaction involving either tetrahedral intermediates or displacement of chloride ion synchronized with bond formation to a methanolic oxygen. In terms of the reaction scheme as we have formulated it, the essentially constant values for the third-order rate coefficient for a given methanol concentration (Table VI), without any marked tendency toward a limiting rate, requires that formation of I be a facile process and the over-all rate be severely restricted by I almost always reverting to reactants.

Briody and Satchell[17] have proposed that reactions of chloroacetyl chlorides with phenols in acetonitrile are essentially SN2 processes with, in the transition state, bond breaking dominant over bond making. This claim has been given support in at least one recent account of acylation mechanisms.[18] We wish to present an alternative explanation of their experimental results which does not require a synchronous mechanism and which involves, in part, a tetrahedral intermediate mechanism. Despite their claim to the contrary, a tetrahedral intermediate mechanism cannot be excluded for these reactions.

Briody and Satchell have claimed that, in phenolysis reactions, unsubstituted acyl halides react by ionization routes but chloroacetyl chloride reacts by a synchronous displacement mechanism. Their argument was largely based upon the observation, for the chloro-substituted compounds only, of a powerful catalysis by tetraethylammonium chloride or bromide. This was interpreted in terms of a mechanism in which bond breaking is assisted by an electrophilic attack at the chlorine by the tetraethylammonium ion. However, the extremely high degree of dissociation of tetraethylammonium chloride in acetonitrile[19] indicates only a very weak affinity of the tetraethylammonium ion for the chloride ion in this solvent and this factor does not support the proposed electrophilic intervention in the reaction, which was formulated.

$$ArOH + RCOCl + M^+Cl^- \longrightarrow$$

$$\underset{H}{\overset{Ar}{\underset{\diagdown}{\diagup}}} \overset{\delta^+}{O} - - - \underset{\overset{\|}{O}}{\overset{R}{C}} - - - \overset{\delta^-}{Cl} - - - M^+Cl^- (\text{or } M^+) \longrightarrow \text{ester} + HCl + M^+Cl^-$$

Unfortunately, parallel studies with a tetraethylammonium salt containing a weakly basic anion, such as perchlorate, were not carried out. One feature which su-

perficially supported the proposed mechanism was that p-methoxyphenolysis of chloroacetyl chloride was accelerated about equally by either tetraethylammonium chloride or tetraethylammonium bromide. However, we find the assumption that bromide ion (a strong nucleophile in acetonitrile) interacts at the acyl carbon of chloroacetyl chloride slower than comparable concentrations of a phenol hard to accept and we favor the setting up of an initial equilibrium.

$$RCOCl + Br^- \Longrightarrow RCOBr + Cl^-$$
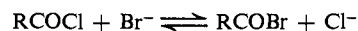
Although this equilibrium will have a tendency to lie to the left, it would be influenced by the at least 40-fold excess of chloroacetyl chloride over tetraethylammonium bromide and the investigated systems were probably complex ones involving chloride ion plus bromide ion catalysis to the p-methoxyphenolysis of chloroacetyl chloride plus chloroacetyl bromide. Apparently, these mixed systems had about the same over-all rate of reaction as the corresponding chloride ion catalyzed p-methoxyphenolysis of chloroacetyl chloride.

Since we found a powerful catalysis by tetraethylammonium chloride in our methanolysis study, but only extremely modest catalysis by tetraethylammonium perchlorate, we propose that the tetraethylammonium halide catalysis observed by Briody and Satchell for the phenolysis of chloroacetyl halide can be explained in a more plausible manner by involving the halide ion and not the tetraethylammonium ion in the reaction scheme and, contrary to their claims, *the catalysis can be explained in terms of tetrahedral intermediates (although it does not demand them) without the need for recourse to a synchronous SN2 type mechanism.*

If unsubstituted acyl halides react entirely by an acylium ion mechanism,[20] then the rate for reaction by this mechanism will be severely reduced on introduction of a chloro substituent. On the other hand, a reaction scheme involving attack on the acyl halide and proceeding through a tetrahedral intermediate, which was swamped out for the unsubstituted compound, will be considerably increased in rate and the gap between the faster rates of the acylium ion routes and the slower rates of the tetrahedral intermediate routes will be narrowed. Under identical conditions, dichloroacetyl chloride has been reported to undergo phenolysis reactions slower than chloroacetyl chloride by at least a factor of 10^2[21] and, provided we accept that on introduction of chloro substituents polar factors are more important than steric factors,[22] it would appear that acylium ion routes still dominate for chloroacetyl chloride. Addition of chloride ion will not be catalytic for reactions *severely* dominated by ionization routes but the increased importance of tetrahedral intermediate routes accompanying introduction of chloro substituents can lead to the need to consider phenolysis reaction schemes of the type which we have outlined, earlier in this paper, for alcoholysis. However, it is to be expected that a reac-

(17) J. M. Briody and D. P. N. Satchell, *J. Chem. Soc.*, 168 (1965).

(18) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, p 274.

(19) I. Y. Ahmed and C. D. Schmulbach (*J. Phys. Chem.*, 71, 2358 (1967)) have found acetonitrile solutions of tetraethylammonium chloride to be completely dissociated for concentrations of up to, at least, 2×10^{-3} M.

(20) This requires that the repressed rate, on addition of chloride ion, involves reaction upon a RCO^+Cl^- ion pair. As pointed out by Briody and Satchell,[17] the similar activation energies for repressed and unrepressed reaction lend some support to this view. With this interpretation, under any given conditions, the rate for chloroacetyl chloride could be lower than the repressed rate for acetyl chloride, as is observed, without any need to propose changes in mechanism.

(21) J. M. Briody and D. P. N. Satchell, *Proc. Chem. Soc.*, 268 (1964).

(22) The relative solvolysis rates, in the order $CHCl_2COCl > CH_2ClCOCl > CH_3COCl$,[21] support this assignment.

Table IX

(A) [PNBC]: 0.0400 M; [MeOH]: 0.0800 M; Temp: 0.0°; Titers in ml of 0.0100 M NEt$_3$ per 5.00-ml Aliquot								
Time, min	0	140	352	420	570	731	870	1230	1380
Titer	0.010	0.158	0.363	0.437	0.587	0.730	0.875	1.207	1.308
$10^4 k_2'$, l. mol^{-1} sec^{-1}		0.111	0.106	0.108	0.108	0.106	0.107	0.106	0.103

(B) [PNBC]: 0.0400 M; [MeOH]: 0.0800 M; [NEt$_4$Cl]: 0.0190 M; Temp: 0.0°; Titers in ml of 0.0200 M NEt$_3$ per 2.00-ml Aliquot						
Time, min	0.00	0.675	1.15	1.73	2.20	2.78
Titer	0.268	0.354	0.418	0.506	0.578	0.634
$10^4 k_2'$, l. mol^{-1} sec^{-1}		74.9	77.6	83.6	86.7	82.2
Time, min	3.23	3.80	4.20	4.70	5.20	
Titer	0.688	0.758	0.800	0.840	0.878	
$10^4 k_2'$, l. mol^{-1} sec^{-1}	82.1	82.5	81.8	79.4	77.5	

(C) [PNBC]: 0.0400 M; [MeOH]: 0.320 M; [PhOH]: 0.640 M; Temp: 25.0°; Titers in ml of 0.0400 M NEt$_3$ per 5.00-ml Aliquot								
Time, min	0	10	20	30	40	50	60	70	80
Titer	0.150	0.280	0.415	0.610	0.685	0.855	0.985	0.995	1.138
$10^4 k_2'$, l. mol^{-1} sec^{-1}		1.41	1.47	1.74	1.53	1.65	1.66	1.44	1.68

tion path involving a second phenol molecule (analogous to reaction *via* (2b)) will be disfavored due to the weak basicity of phenol. In particular, one should not be surprised if a chloride ion catalyzed reaction path proceeding through a tetrahedral intermediate (analogous to reaction *via* (2c)) can make a significant contribution to the over-all reaction.

The acceleration observed for addition of 0.0183 M tetraethylammonium chloride to the reaction of 0.01 M p-methoxyphenol with chloroacetyl chloride can be estimated by interpolation as 150-fold, compared to a larger, 3450-fold, acceleration for an identical addition to the reaction of 0.01 M methanol with p-nitrobenzoyl chloride. While the relative chloride ion induced accelerations of different reactions passing through a tetrahedral intermediate would not be expected to be identical, the magnitudes of these ratios do lend some support to the proposal of pronounced chloride ion catalysis to a phenolysis reaction even when the catalysis operates upon a tetrahedral intermediate reaction path which contributes only a very small proportion to the over-all uncatalyzed phenolysis reaction rate.

Experimental Section

Materials. Acetonitrile (Mallinckrodt "Nanograde") was purified as described previously.[13,23] Nitromethane (Eastman "Spectrograde"), purified using the method reported by Olah, Kuhn, Flood, and Hardie,[24] was kindly provided by Mr. V. V. Likhite. p-Nitrobenzoyl chloride (Eastman) was purified by adding 25 g to 50 ml of petroleum ether (60–110° boiling range) and warming until boiling commenced. The hot solution was filtered and p-nitrobenzoyl chloride recovered by cooling to ice temperature. The pale yellow crystals were collected on a Büchner funnel and immediately transferred to a round-bottomed flask and dried by suction, using a vacuum pump, for about 8 hr. The dried crystals, mp 73.5–74.0° (lit. 73°,[25] 75°[26]), were stored in a vacuum desiccator over calcium chloride.

Especially for runs at low methanol concentrations, high purity of both p-nitrobenzoyl chloride and methanol was a prerequisite. The most relevant test for purity was the rate of acid development in a run carried out in the absence of methanol. A first-order rate

coefficient for acid production of less than 5×10^{-8} sec^{-1} at 25.0° was considered acceptable; this background constituted less than 10% of the rate of acid production for reaction in the presence of 0.01 M methanol. In most cases the background was somewhat less than this value and the lowest specific rate of acid production obtained for any combination of acetonitrile and p-nitrobenzoyl chloride was 1.2×10^{-8} sec^{-1}. For runs in nitromethane, the corresponding background specific rate was about 0.5×10^{-8} sec^{-1}.

Methanol (Baker AR) was used without further purification. Phenol (Baker AR) was purified by warming 80 g with 100 ml of petroleum ether (30–60° boiling range) until two layers separated. The petroleum ether layer was cooled until crystals of phenol separated. After filtration these crystals were dried under vacuum and stored in capped containers within a vacuum dessicator. Tetraethylammonium perchlorate (Eastman) was recrystallized from water and dried using a vacuum pump; tetraethylammonium chloride (Eastman) was recrystallized from acetone and similarly dried. Because the chloride salt was extremely hygroscopic, it was necessary to perform transfers in a dry atmosphere, stopper tightly, weigh, and immediately add the requisite volume of solvent.

For runs carried out in the presence of added tetraethylammonium salts, appropriate blanks were carried out by exclusion of methanol. Addition of the perchlorate salt led to a modest acceleration of the blank rate of acid production, approximately paralleling its effect upon the methanolysis rates. Addition of the chloride salt led to fairly large rate increases within the blank experiments but, because the methanolysis rates are also subject to powerful catalysis by added chloride ion, in no instance was the background rate greater than 1.5% of the over-all reaction rate in the presence of added methanol.

Kinetic Methods. All glassware used in the preparation of solutions for kinetic runs and in removal of samples was oven baked for several hours before use. The acid produced at suitable time intervals during the course of reaction was determined by pipeting 2- or 5-ml aliquots from bulk solution and quenching in 20 or 30 ml of acetone maintained at solid CO$_2$–acetone slush temperature. The acid produced was titrated against a standardized solution of triethylamine in toluene to a resorcinol blue (Lacmoid) end point. Although traces of adventitious chloride would be expected to cause a large acceleration to runs in the absence of added tetraethylammonium chloride, especially at low methanol concentrations, this acceleration would be of short duration due to hydrogen chloride produced in the reaction deactivating the chloride ion by complexing to give the hydrogen dichloride anion. No unusually high initial rates were detected and any perturbations due to adventitious chloride ion catalysis were, therefore, within experimental error.

In the three illustrative runs which follow, the second-order rate coefficients for acid production are first order with respect to p-nitrobenzoyl chloride (PNBC) and first order with respect to methanol (Table IX).

(23) D. N. Kevill and J. E. Dorsey, *J. Org. Chem.*, **34**, 1985 (1969).

(24) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, *J. Amer. Chem. Soc.*, **86**, 1039 (1964).

(25) R. Adams and R. L. Jenkins, "Organic Syntheses," 2nd ed, Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1948, p 394.

(26) J. R. A. Pollock and R. Stevens, Ed., "Dictionary of Organic Compounds," 4th ed, Eyre and Spotiswoode (Publishers) Ltd., London, 1965, p 2438.