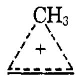
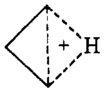
The above results confirm further the previously drawn conclusion[3] that the corner-protonated cyclopropane IV—if involved in these reactions—does not precede the edge-protonated cyclopropane V in the reaction. Had it done so, the 1-propanol-2,2-d_2 would have produced extensively isotope-position rearranged, mainly I, 1-chloropropane.



IV



V

The nonintervention of protonated cyclopropanes in the reaction of 1-chloropropane with aqueous silver nitrate is consonant with our previous finding that no protonated cyclopropanes intervene in the analogous reaction of 1-bromopropane with silver nitrate.[3]

Experimental Section

Synthesis of Labeled Compounds. The 1-propanol-1,1-d_2 was prepared by reduction of propionic anhydride with lithium aluminum deuteride. The 1-propanol-2,2-d_2 was prepared by repeated exchange of methylmalonic acid with deuterium oxide, decarboxylation of this acid to propionic acid, and reduction of the propionic acid with lithium aluminum hydride.

Trimethylsilyl ether derivatives of the alcohols were prepared by warming overnight a 2:1 molar mixture of the alcohol and hexamethyldisilazane (Metallomer Laboratories) with a drop of trimethylchlorosilane. Purification was achieved by gas chromatography on a 20 ft × 1/4 in. 20% Carbowax 20M on 60–80 Chromosorb W column at 60–80°.

Reactions of 1-Propanols with Thionyl Chloride in Pyridine. To a mixture of 1-propanol (0.1 mol) and pyridine (0.1 mol) was added slowly, under cooling, thionyl chloride (0.4 mol). The mixture was then heated to reflux for 45 min. About 5.3 g (69%) of 1-chloropropane was obtained which was shown by gas chromatography to be uncontaminated by any 2-chloropropane (less than 0.2%). The reactions of the labeled propanols gave similar results.

Reactions of 1-Propanols with Zinc Chloride and Hydrochloric Acid. To 18 ml of concentrated hydrochloric acid was dissolved, under cooling, 27.2 g (0.2 mol) of zinc chloride which had been heated to melting under vacuum (0.1 mm). To this solution was added 7.5 ml (0.1 mol) of 1-propanol. The apparatus, which was fitted with jacketed column, thermometer and condenser, was heated to 130–140°. The chloropropane product (70% yield) consisted (gas chromatography) of 89% 1-chloropropane and 11% 2-chloropropane. Under identical conditions 1-propanol-1,1-d_2 gave 89% 1-chloropropane and 11% 2-chloropropane, whereas 1-propanol-2,2-d_2 gave 95% 1-chloropropane and 5% 2-chloropropane.

Reactions of 1-Chloropropanes with Zinc Chloride and Hydrochloric Acid. To a solution of 10 g (0.08 mol) of fused, anhydrous zinc chloride in 7 ml (0.08 mol) of concentrated hydrochloric acid was added 3 g (0.038 mol) of 1-chloropropane that was prepared by the reaction of 1-propanol with thionyl chloride in pyridine. The reaction flask, which was fitted with a long reflux condenser (Grahm type) stoppered tightly at the top, was heated at 50° for 72 hr. The recovered chloropropane (34%) was shown by gas chromatography to consist only of 1-chloropropane (less than 0.2% 2-chloropropane). The labeled 1-chloropropanes gave similar results.

Reactions of 1-Chloropropanes with Silver Nitrate. To a solution of 7.6 g (0.045 mol) of silver nitrate in 50 ml of water was added 3 g (0.038 mol) of 1-chloropropane. The mixture was stirred for 4 days at room temperature, and in the absence of light. After filtration of the silver chloride, saturation of the aqueous solution with potassium fluoride and extraction with ether, 0.9 g (40% yield) of 1-propanol (less than 0.2% 2-propanol by gas chromatography) was obtained. The labeled 1-chloropropanes gave similar results.

Mass spectra of the trimethylsilyl ethers were measured with 70-V electrons on a Consolidated Model 21-103C instrument.

Acknowledgment. We thank the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, for support of the research carried out at Michigan State University.

(1968). From the reaction of 1-propanol-1-t with zinc chloride and hydrochloric acid they obtained about 1% isotope-position rearranged 1-chloropropane, which compares favorably with our 1.5–1.8% rearranged product. They, however, found the rearranged label to be about equally distributed between positions 2 and 3.

Evidence for Hydrogen-Bonded Transition States in the Rate-Determining Step of the Reaction of Benzoyl Chlorides with Ethanol in Acetone and Chloroform

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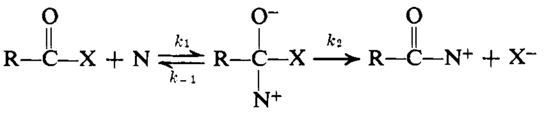
Received February 25, 1970

Abstract: The reactions of benzoyl chloride and mononitrobenzoyl chlorides with ethanol in acetone are mixed second- and third-order reactions. In chloroform the reaction of ethanol with o-nitrobenzoyl chloride is also mixed second and third order, but the reaction of p-nitrobenzoyl chloride is third order only. These results can be rationalized by assuming that every rate-determining transition state contains the substrate, the nucleophile, ethanol, and an acceptor for hydrogen bonding. Suitable acceptors are another ethanol molecule, an acetone molecule, and a chloride ion.

The reactions of carboxylic acid derivatives, which entail a substitution at the carbonyl carbon atom, almost invariably proceed through an addition–elimination mechanism, in the first step of which the carbonyl carbon atom assumes a tetrahedral configuration.[1] The general mechanism may be written as follows,



$$R-\overset{\overset{O}{\|}}{C}-X + N \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R-\underset{\underset{N^+}{|}}{\overset{\overset{O^-}{|}}{C}}-X \xrightarrow{k_2} R-\overset{\overset{O}{\|}}{C}-N^+ + X^-$$

where N is the nucleophile and X is the leaving group.

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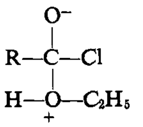
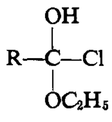
[1] M. L. Bender, *Chem. Rev.*, 60, 53 (1960).

For the ethanolysis of an acid chloride, where the nucleophile is ethanol and the leaving group is a chloride ion, it can be asserted, with considerable certainty, that k_2, in the reaction scheme above, is much greater than k_{-1}, since both ethanol and ethoxide ion are much poorer leaving groups than chloride ion. It follows, therefore, that the rate constants obtained for this reaction are determined by the preliminary bond-forming process and measure the rate of formation of the intermediate, which, for this case, may be represented by I or II.



$$R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H-\overset{+}{O}-C_2H_5}{|}}{C}}-Cl$$

I



$$R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OC_2H_5}{|}}{C}}-Cl$$

II

From the foregoing discussion, it would be anticipated that the rate of reaction of an acid chloride with an alcohol in an aprotic solvent is second order, first order in the acid chloride, and first order in the alcohol. Actual measurements of reaction rates indicate that the reaction is, in fact, more complex. No case of simple second-order rates for this reaction has been observed, and the reported orders in alcohol concentration have included second order,[2,3] mixed first and second order,[4] and even mixed first, second, and third order.[5]

These results raise some doubts about the correctness of the preconceptions with respect to the mechanism of this reaction. The present study was undertaken to explore these difficulties. It includes measurements of the rate of reaction of benzoyl chlorides with ethanol at 24.8 ± 0.1° in two aprotic solvents, acetone and chloroform. Acetone was chosen, since it is a good acceptor for hydrogen bonding but an ineffective donor. For modest concentrations of ethanol in this solvent, it is to be expected that the preferred mode of hydrogen bonding would be from alcohol as donor to acetone as acceptor. Chloroform, on the other hand, is a suitable donor for hydrogen bonding but a poor acceptor. In this solvent, too, it was hoped that alcohol–alcohol hydrogen bonding would be minimized. The pertinence of these considerations will be made apparent in the Discussion.

Results

The rates of reaction of benzoyl chloride and the three mononitrobenzoyl chlorides with ethanol in acetone at 24.8 ± 0.1° are collected in Table I. Individual runs afford excellent second-order plots, but, with every substrate, the observed rate constants, at a constant initial concentration of the acid chloride, increase markedly with increasing initial concentrations of alcohol. As shown in Figure 1, plots of k_2^*, the measured second-order rate constant, *vs.* the initial ethanol concentrations are linear and show positive intercepts on the *Y* axis. These results can be fitted with eq 1, and the values of k_2 and k_3, compiled in Table II, may be obtained from the intercepts and slopes, respectively, of the linear plots shown in Figure 1.

$$k_2^* = \frac{d[Cl^-]}{dt} \times \frac{1}{[ROH][R\text{-}CO\text{-}Cl]} = k_2 + k_3[ROH] \qquad (1)$$

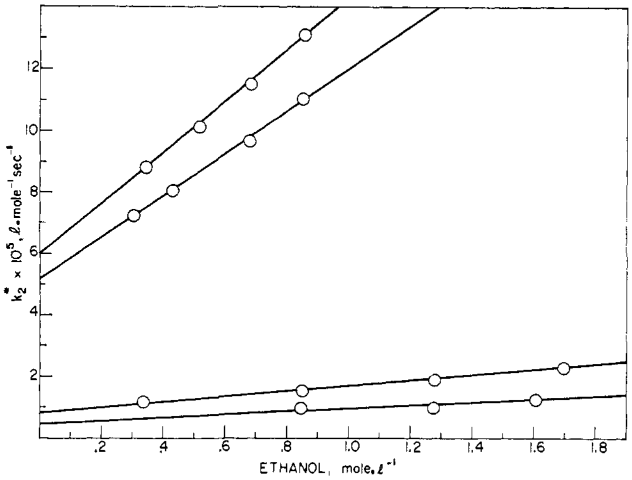


Figure 1. A plot of k_2^* *vs.* the initial ethanol concentrations for the ethanolysis of benzoyl chlorides in acetone. The straight lines are, reading from top to bottom, for *p*-nitrobenzoyl chloride, *m*-nitrobenzoyl chloride, *o*-nitrobenzoyl chloride, and benzoyl chloride.

Table I. Rates of Reaction of Benzoyl Chlorides with Ethanol[a]

[RCl], mol l.$^{-1}$	[ROH], mol l.$^{-1}$	$k_2^* \times 10^5$, l. mol^{-1} sec^{-1}
	Benzoyl Chloride	
0.0858	0.848	0.978
0.0856	1.27	1.08
0.0845	1.61	1.29
	o-Nitrobenzoyl Chloride	
0.0750	0.338	1.17
0.0745	0.846	1.52
0.0743	1.29	1.90
0.0752	1.69	2.33
	m-Nitrobenzoyl Chloride	
0.0535	0.301	7.23
0.0520	0.423	8.07
0.0531	0.680	9.69
0.0515	0.849	11.1
	p-Nitrobenzoyl Chloride	
0.0523	0.338	8.81
0.0558	0.510	10.1
0.0547	0.677	11.5
0.0540	0.849	13.1

[a] In acetone at 24.8 ± 0.1°.

Table II. Values of k_2 and k_3[a]

Acid chloride	$k_2 \times 10^5$, l. mol^{-1} sec^{-1}	$k_3 \times 10^5$, l.^{2} mol^{-2} sec^{-1}	k_3/k_2, l. mol^{-1}
Benzoyl chloride	0.40	0.53	1.3
o-Nitrobenzoyl chloride	0.80	0.89	1.1
m-Nitrobenzoyl chloride	5.2	6.8	1.3
p-Nitrobenzoyl chloride	6.0	8.2	1.4

[a] Obtained from plots of k_2^* *vs.* [EtOH], for the ethanolysis of benzoyl chlorides in acetone at 24.8 ± 0.1°.

In chloroform as the solvent, *o*-nitrobenzoyl chloride shows a behavior similar to that found in acetone. As shown in Table III, the values of k_2^* increase with increasing initial ethanol concentrations. A plot of k_2^* *vs.* initial alcohol concentration is linear and gives a

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(2) A. A. Ashdown, *J. Amer. Chem. Soc.*, **52**, 268 (1930).
(3) W. R. Gilkerson, *J. Phys. Chem.*, **60**, 1142 (1956).
(4) D. N. Kevill and F. D. Foss, *J. Amer. Chem. Soc.*, **91**, 5054 (1969).
(5) R. F. Hudson and B. Saville, *J. Chem. Soc.*, 4121 (1955).

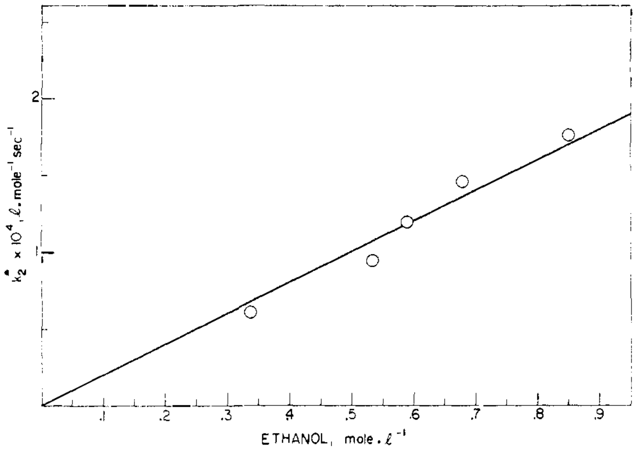

Figure 2. A plot of k_2^* *vs.* the initial ethanol concentrations for the ethanolysis of *p*-nitrobenzoyl chloride in chloroform.

positive intercept. The results can be accommodated by eq 1, with k_2 equal to 0.66×10^{-5} l. mol^{-1} sec^{-1} and k_3 equal to 1.48×10^{-5} l.^{2} mol^{-2} sec^{-1}.

With *p*-nitrobenzoyl chloride a significantly different behavior mode was observed (Table III). The values of k_2^* again increase as the initial alcohol concentrations increase. A plot of k_2^* *vs.* initial ethanol concentration, shown in Figure 2, is linear, but the best straight line through the experimental points would result in a negative intercept. However, the experimental results can be fitted, well within experimental error, by a straight line going through the origin.

Table III. Rates of Reaction of Benzoyl Chlorides with Ethanol[a]

[RCl], mol l.$^{-1}$	[ROH], mol l.$^{-1}$	$k_2^* \times 10^5$, l. mol^{-1} sec^{-1}	$k_3 \times 10^4$, l.^{2} mol^{-2} sec^{-1}
	o-Nitrobenzoyl Chloride		
0.0745	0.848	1.92	
0.0744	1.36	2.68	
0.0747	1.68	3.13	
	p-Nitrobenzoyl Chloride		
0.0542	0.338	6.04	1.89
0.0540	0.533	9.42	1.85
0.0540	0.591	12.0	2.12
0.0597	0.679	14.6	2.22
0.0540	0.848	17.6	2.15

[a] In chloroform at 24.8 ± 0.1°.

Equation 1 is appropriate only with k_2 equal to zero. The overall reaction order is not mixed second and third order, as found in all the other rates measured, but pure third order. This conclusion has been verified by calculating third-order rate constants for this reaction using eq 2, where A_0 is the initial concentration of acid

$$\frac{1}{(A_0 - B_0)}\left[\frac{1}{(B_0 - x)} + \frac{2.303}{(A_0 - B_0)}\log\frac{(B_0 - x)}{(A_0 - x)}\right] = k_3t + \frac{1}{(A_0 - B_0)}\left[\frac{1}{B_0} + \frac{2.303}{(A_0 - B_0)}\log\frac{B_0}{A_0}\right] \qquad (2)$$

chloride, B_0 is the initial concentration of ethanol, and x is the concentration of chloride ion formed at time, t. The individual values of k_3 that were obtained are shown in the last column of Table III. The average value is 2.05×10^{-4} l.^{2} mol^{-2} sec^{-1}, and the average deviation from this value is less than 7%. This value is, furthermore, identical within experimental error, with the slope of the straight line drawn through the experimental points in Figure 2.

The addition of benzyltriethylammonium nitrate has a profound effect on both the rate and course of these reactions. An acetone solution which was 0.053 *M* in *p*-nitrobenzoyl chloride, 0.34 *M* in ethanol, and 0.014 *M* in the nitrate liberated 54% of its chloride ion in 0.5 hr and 75% in 1 hr. The same concentrations of the acid chloride and ethanol, in the absence of the salt, required 9 hr to liberate 60% of the chloride ion. The final product of this reaction was ethyl-*p*-nitrobenzoate, isolated as a crude product, mp 51–55°, in quantitative yield and as a recrystallized product, mp 54–56°, in 80.6% yield.

The addition of benzyltriethylammonium nitrate to the reaction with benzoyl chloride causes a definite but less dramatic acceleration of the rate. In the presence of 0.020 *M* nitrate, a solution, 0.086 *M* in benzoyl chloride and 0.85 *M* in ethanol, liberates 30% of the ionic halogen in less than 3 hr. In the absence of the salt, more than 12 hr are required to attain the same extent of reaction. The products, with the salt present, are ethyl benzoate and benzoic acid.

p-Nitrobenzoyl chloride will react with benzyltriethylammonium nitrate even when ethanol is absent. A solution of 0.058 *M* *p*-nitrobenzoyl chloride and 0.056 *M* salt in chloroform turns bright, orange-yellow immediately and liberates 69% of the available chloride ion in 0.5 hr and 94% chloride ion in 2 hr. In these reactions nitrate ion is acting as a nucleophile and reacts with the acid chloride to form, initially an acyl nitrate, which may then solvolyze to form the ethyl ester, if ethanol is present, and/or decompose to form the acid anhydride. The more rapid chloride ion liberation in the presence of the salt results from the fact that nitrate ion is a much more effective nucleophile than ethanol.[6] To the extent that addition of the nitrate leads to a more rapid reaction and still gives ethyl ester as the final product, this is a case of nucleophilic catalysis.

Experimental Section

Materials. Reagent grade acetone was dried over calcium chloride and distilled through a Vigreux column before use. A middle cut, bp 56°, was taken.

Reagent grade chloroform was shaken with 25% of its volume of concentrated sulfuric acid, washed twice with water, dried over calcium chloride, and distilled just before use.

Absolute ethanol was used without purification.

Eastman benzoyl chloride was distilled before use, and a middle cut, bp 83° (18 mm), was collected.

o-Nitrobenzoyl chloride was prepared from *o*-nitrobenzoic acid by treating it with thionyl chloride. The product was twice distilled and had bp 155–156° (15 mm).

m-Nitrobenzoyl chloride was crystallized two times from hexane–benzene; mp 32–33°.

p-Nitrobenzoyl chloride was crystallized to a constant mp of 71–73° from hexane–benzene (four crystallizations).

Benzyltriethylammonium nitrate was prepared either by treating benzyltriethylammonium chloride with silver nitrate or by converting benzyltriethylammonium bromide to the hydroxide with silver oxide and then neutralizing with nitric acid; mp 106–108° (from ethanol–ether).

Rate Measurements. Separate, determinate solutions of the alcohol and acid chloride were made up at the temperature of the measurements. The solutions were mixed at zero time, and ali-

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[6] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 75, 141 (1953).

quots (10 ml) were withdrawn at appropriate time intervals and partitioned between benzene (70 ml) and 1:4 nitric acid (20 ml). The aqueous layer was analyzed for chloride ion by the Volhard method. Each run involved six or more points and was followed to beyond 60% reaction. The bimolecular rate constants were determined from the slopes of log $[A_0(B_0 - x)]/[B_0(A_0 - x)]$ *vs.* t plots, where A_0 is the initial acid chloride concentration, B_0 the initial alcohol concentration, and x the concentration of chloride ion at time, t.

Product Isolation. *p*-Nitrobenzoyl chloride (2 g; 0.0108 mol) in a mixture of acetone (95 ml) and ethanol (5 ml) was left standing at room temperature for 3 days. The solvents were removed and the crude ethyl-*p*-nitrobenzoate was crystallized from ethanol; yield, 1.7 g (80.6%); mp 49–50°. Recrystallization from ethanol–water raised the mp to 55–57°.

A solution of *p*-nitrobenzoyl chloride (2.0 g; 0.0108 mol) and benzyltriethylammonium nitrate (2.0 g; 0.00786 mol) in acetone (95 ml) and ethanol (5 ml) was left standing at room temperature overnight. The solution was taken up in ether (1 l.), washed with 2 portions of water (200 ml), and dried over magnesium sulfate. Removal of the ether gave ethyl *p*-nitrobenzoate, mp 51–55°, in quantitative yield. Crystallization from ethanol–water yielded 1.7 g (80.6%); mp 54–56°.

A solution of benzoyl chloride (6.09 g; 0.043 mol) and benzyltriethylammonium nitrate (5.0 g; 0.0197 mol) in acetone (190 ml) and ethanol (10 ml) was kept at room temperature for 4 days. The solution was taken up in ether (750 ml), washed with 2 portions of water (200 ml), and dried over magnesium sulfate. For vpc analysis the solution was concentrated to 100 ml. The products found were 4.0 g (61.9%) of ethyl benzoate and 1.0 g (19%) of benzoic acid.

A solution of *p*-nitrobenzoyl chloride (2 g; 0.0108 mol) and benzyltriethylammonium nitrate (3 g; 0.0118 mol) in chloroform (100 ml) was left standing at room temperature for 24 hr. The solution was taken up in benzene (300 ml), washed with two 150-ml portions of water, and dried over magnesium sulfate. Removal of the solvent and crystallization from water yielded 1.5 g (83.3%) of *p*-nitrobenzoic acid; mp 238–240°.

Discussion

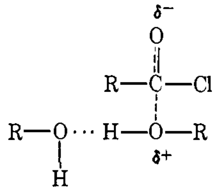
If, as seems eminently reasonable, it must be assumed for the alcoholysis of a benzoyl chloride in an aprotic solvent (i) that the reaction involves the initial formation of an addition intermediate, (ii) that this intermediate proceeds to product much more rapidly than it reverts to starting materials, and (iii) that the measured reaction rates reflect only the bond-forming and not the bond-breaking process, then the crucial question of mechanism becomes whether or not these requirements can be reconciled with the observation that, in every case studied, these reactions require rate equations that contain at least one term which is second order in alcohol concentration.

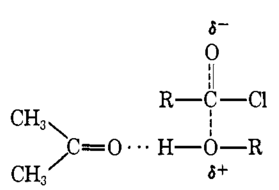
To this question we now address ourselves. For purpose of discussion, it is assumed that the rates measured have been rates of intermediate formation. For all of the substrates studied in acetone, two intermediate-forming transition states are required. One involves a single alcohol molecule, and the other has two alcohols. This is also true for the reaction of *o*-nitrobenzoyl chloride in chloroform, but for *p*-nitrobenzoyl chloride a single transition state, containing two ethanol molecules, is sufficient.

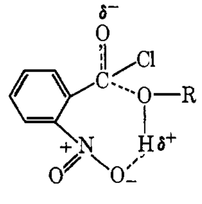
This change from two product-forming transition states to a single one for this last reaction is informative. It should be remembered that the alcoholysis of an acid chloride involves, at some stage along the path from reactants to ester, a proton transfer. This proton transfer can occur in the first step in which the intermediate is formed, in a separate step, after the intermediate is formed but before it is converted to product, or in the final ester-forming step. In accordance with the assumptions that have been made, the measured rates will reflect this proton transfer only if it occurs in the first intermediate-forming step. If it occurs in a separate step, it is probably fast and reversible, since the transfer is from oxygen. If it happens in a concerted step with loss of the leaving group, this step will, in any case, be fast with respect to reversal of the intermediate to starting materials.

Since a proton must be transferred at some stage of the reaction, it is possible that a proton acceptor is involved in the very first step of the reaction. In fact, all of the present results can be rationalized by taking the position that all of the intermediate-forming transition states involve the substrate, a nucleophile, and a proton- or hydrogen-bond acceptor and that, furthermore, this is true even for those transition states which correspond to the second-order terms in the rate equation.

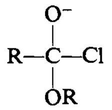
For the reactions in acetone, transition states, III and IV, with III corresponding to the third-order term in the rate equation and IV responsible for the second-order term, are possible. With *o*-nitrobenzoyl chloride still a third transition state, V, is possible, since the *o*-nitro group is suitably positioned to participate in hydrogen-bond formation. In chloroform as solvent a transition state comparable to IV is no longer possible, since chloroform cannot function as an acceptor in hydrogen bonding. With *p*-nitrobenzoyl chloride in this solvent the only possible transition state is III, and the rate equation contains a single third-order term. With *o*-nitrobenzoyl chloride in chloroform, transition state V is again possible and may even be favored, and the rate equation again has two terms, one second order and one third order.

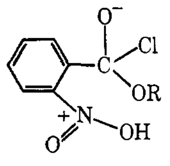

III


IV


V

If the proton transfer occurs in the first step, III and IV would collapse to VI and the conjugate acids of ethanol and acetone, respectively, and V would form VII. The above reactions are completely consistent with the observed rates and their dependence on ethanol concentration. Since the proton transfer in this scheme occurs from oxygen to oxygen in a hydrogen-bonded complex, a zero or small deuterium isotope effect would

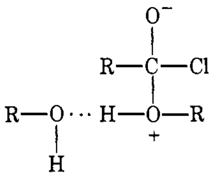

$$\mathrm{R{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle OR}{\underset{|}{C}}}}{-}Cl}$$
VI



VII

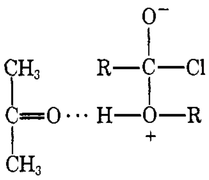
be predicted for this reaction according to Swain's "solvation rule."[7]

It is not essential to the presently proposed mechanism that the proton transfer occur in this first step. It is possible that the intermediate is a hydrogen-bonded complex, *i.e.*, that III, IV, and V give VIII, IX, and X, respectively. The proton transfer could then occur in a fast, reversible separate step or in the ester-forming step. In neither case would these processes be reflected in the measured rates, and the present results, therefore, permit no decision as to the actual timing of the proton-transfer step. Within the assumptions made and the limitations imposed, all three possibilities for the proton transfer are consistent with the observed rates.



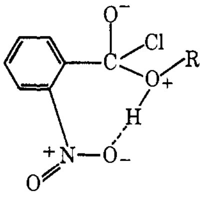
$$\mathrm{R{-}\underset{\substack{|\\ H}}{O}\cdots H{-}\underset{+}{O}{-}R},\quad \mathrm{R{-}\overset{\substack{O^-\\ |}}{C}{-}Cl}\ \text{bonded to the O}^+$$

VIII



$$\mathrm{(CH_3)_2C{=}O\cdots H{-}\underset{+}{O}{-}R},\quad \mathrm{R{-}\overset{\substack{O^-\\ |}}{C}{-}Cl}\ \text{bonded to the O}^+$$

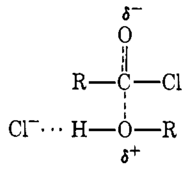
IX



X

Mechanisms involving hydrogen-bonded transition states in the rate-determining step appear to have some generality. Such transition states best account for the modest base catalysis observed in the reactions of 2,4-dinitrochlorobenzene with primary and secondary amines[8] and afford the best explanation of the observed rates in the reaction of phenacyl bromide with N-ethylaniline in chloroform[9] even though this latter reaction is probably synchronous and does not involve an intermediate. Both of these reactions require a proton transfer at some point along the reaction path. The reactions of both 2,4-dinitrochlorobenzene[10] and phenacyl bromide[9] with tertiary amines, on the other hand, are straightforward, bimolecular reactions, since a proton transfer is not involved.

In the above reactions, a study of the effect of an added quaternary ammonium nitrate on the reaction rates proved to be a useful diagnostic technique. For the reaction of an acid chloride and alcohol, this approach is not fruitful, since nitrate ion is a more efficient nucleophile than ethanol and reacts relatively rapidly with the acid chloride to form what is almost certainly the acyl nitrate. This difficulty was avoided in the studies of the catalytic effect of an added quaternary ammonium chloride reported by Kevill and Foss,[4] since, when chloride ion reacts as a nucleophile, it merely regenerates the starting material. The observed catalysis is in accord with the present formulation, since, in acetonitrile, chloride ion can function as an acceptor in hydrogen bonding. An appropriate rate-determining transition state would be XI. A mechanism in which the acid chloride and ethanol first react to give I or II, which undergoes a subsequent deprotonation step with chloride ion to give VI, is inappropriate. This separate proton-transfer step is almost certainly fast and reversible, since it involves proton removal from oxygen. For this mechanism, therefore, the observed rates would depend only on the acid chloride and ethanol concentrations and would be independent of the concentration of added chloride ion.



$$\mathrm{Cl^-\cdots H{-}\underset{\delta+}{O}{-}R},\quad \mathrm{R{-}\overset{\substack{\delta-\\ O\\ \|}}{C}{-}Cl}\ \text{partially bonded to the O}$$

XI

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(8) S. D. Ross, *Tetrahedron*, **25**, 4427 (1969).

(9) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Amer. Chem. Soc.*, **90**, 6411 (1968).

(10) S. D. Ross and M. Finkelstein, *ibid.*, **79**, 6547 (1957).