[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Kinetics of the Reaction of Benzoyl Halides with Toluene in Non-polar Solvents under the Influence of Aluminum Halides[1,2]

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Kinetic studies have been made of the reaction of benzoyl chloride with toluene, under the influence of aluminum chloride, in 1,2,4-trichlorobenzene, *o*-dichlorobenzene, methylene chloride and ethylene chloride as solvents. The rate constants vary with the solvent, increasing with solvent in the order indicated. The reactions are first order in toluene, first order in the benzoyl chloride–aluminum chloride complex, and independent of the concentration of excess benzoyl chloride. The calculated rate constants increase linearly with increasing initial concentration of the benzoyl chloride–aluminum chloride complex, presumably a "salt effect" of the dipolar addition complex. For ethylene chloride solutions 0.1 *M* in the complex, the rate constants are (10^{-3} l. mole^{-1} sec.$^{-1}$) 0.0874 at 0.0°, 0.763 at 25.0° and 1.59 at 35.0°, leading to an enthalpy of activation of 13.35 kcal. mole^{-1} and an entropy of activation of −28.1 e.u. To permit independent variation of the aluminum halide, a related study was made of the kinetics of reaction of benzoyl bromide with toluene in the presence of aluminum bromide in 1,2,4-trichlorobenzene as solvent. This reaction is also first order in toluene and first order in benzoyl bromide–aluminum bromide, with the second-order rate constant increasing with increasing concentration of the complex. Under similar conditions the rate constant is only 20% greater than for the corresponding reaction involving benzoyl chloride–aluminum chloride. With aluminum bromide present in excess over the concentration of benzoyl bromide, the rate of the reaction is greatly increased, and at high concentrations the reaction follows third-order kinetics.

The present program of study of the Friedel–Crafts acylation reaction was undertaken with two major objectives. We hoped to utilize the reaction to obtain quantitative data on the effects of substituents on the rates of aromatic substitutions, and to compare the effectiveness of various Lewis acids as catalysts in typical Friedel–Crafts reactions.

In the initial stage of this program, we obtained kinetic data on the aluminum chloride-catalyzed reaction of benzoyl chloride with various aromatic hydrocarbons in nitrobenzene solution.[6,7] Unfortunately, kinetic complications were encountered in this solvent.[8]

The use of benzoyl chloride as a solvent resulted in simple second-order kinetics and the system was applied to the determination of the partial rate factors in the benzoylation of representative benzene derivatives[9] and to the study of the effect of various Friedel–Crafts catalysts on the rate.[10]

Unfortunately, the procedure required exhaustive purification of the benzoyl chloride and a relatively tedious method for following the rate, isolating and weighing the product. Moreover, since the reactant benzoyl chloride also served as solvent medium, it prevented examination of other acid chlorides under conditions where the data would be comparable. For these reasons, it appeared desirable to explore the possibility of utilizing other, inert solvents for the reaction medium.

The kinetics of the Friedel-Crafts acylation reaction in nonpolar solvents has been investigated previously by a number of workers.[11–15] In general, these workers agree that the reaction is first order in the benzoyl chloride–aluminum chloride complex and first order in the aromatic hydrocarbon. Using the reactant benzene as solvent at 35°, it has been reported recently that the calculated rate constant is essentially independent of the initial concentration of the complex.[15] However, the earlier studies, using benzene as solvent at 30°,[12,14] toluene as solvent[11,13] or carbon disulfide as solvent,[12] are all in agreement that the calculated rate constants increase with increasing initial concentrations of the complex. In the latter studies the rate constant increased from 15 to 30% for a twofold increase in the initial concentration of the complex. It has also been noted that the excess aluminum halide (over the stoichiometric quantity required to form the benzoyl halide complex) possesses a marked catalytic effect on the acylation reaction. On the other hand, excess benzoyl halide has no effect on the reaction rate, and the ketone is formed irreversibly.[11,12,14]

Practically all of these earlier studies were carried out in excess aromatic hydrocarbon as solvent or in carbon disulfide. The former expediency was undesirable for one of our objectives. Carbon disulfide possesses a number of undesirable properties for kinetic work. Moreover, it appeared possible that we might avoid or minimize the variation in rate constant with initial concentration of the complex by a judicious choice of solvent. Accordingly, we undertook a kinetic examination of the reaction of benzoyl chloride with a representative aromatic, under the influence of aluminum chloride, in 1,2,4-trichlorobenzene, *o*-dichlorobenzene,

(1) The Catalytic Halides. XXV. Directive Effects in Aromatic Substitution. XXXI.

(2) Based in part upon a thesis submitted by F. R. Jensen in partial fulfillment of the requirements for the Ph.D. degree.

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(4) Research assistant, 1953–1954, on project no. AT(11-1)-170 supported by the Atomic Energy Commission. National Science Foundation Predoctoral Fellow, 1954–1955.

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(6) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 724 (1957).

(7) H. C. Brown, B. Bolto and F. R. Jensen, *ibid.*, **23**, 414, 417 (1958).

(8) N. N. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **24**, 664 (1954), has observed complex kinetics in the alkylation of benzene catalyzed by aluminum chloride in nitrobenzene.

(9) H. C. Brown and F. R. Jensen, THIS JOURNAL, **80**, 2291, 2296 (1958).

(10) F. R. Jensen and H. C. Brown, *ibid.*, **80**, 3039 (1958).

(11) B. D. Steele, *J. Chem. Soc.*, **83**, 1470 (1903).

(12) S. C. J. Olivier, *Rec. trav. chim.*, **37**, 205 (1918).

(13) L. F. Martin, P. Pizzolato and L. S. McWaters, Jr., THIS JOURNAL, **57**, 2584 (1935).

(14) H. Ulich and P. V. Fragstein, *Ber.*, **72**, 620 (1939).

(15) F. Smeets and J. Verhulst, *Bull. soc. chim. Belg.*, **63**, 439 (1954).

methylene chloride and ethylene chloride. Since toluene proved to react at a convenient rate at room temperature, it was utilized as the aromatic in these experiments. The study was extended to include the related reaction of aluminum bromide and benzoyl bromide with toluene in 1,2,4-trichlorobenzene as solvent.

Results

Benzoyl Chloride–Aluminum Chloride.—The benzoyl chloride–aluminum chloride complex was prepared by dissolving the two components in the carefully purified solvents. The rates were followed by measurement of the residual benzoyl chloride in aliquots of the reaction solutions.

In individual experiments the rates exhibited simple second-order kinetics. The second-order rate constants were calculated from the appropriate integrated form of the rate expression

$$\text{rate} = k_2[C_6H_5CH_3][C_6H_5COCl\cdot AlCl_3]$$

In the initial exploratory experiments, we were content with a precision of ±5% in the rate constants. These data are summarized in Table I, with the rate constants rounded off to two significant figures. We then adopted ethylene dichloride as the reaction medium of preference and made a more detailed study, with higher precision, ±2%, of the effects of varying the concentrations of the reactants. These data are summarized in Table II.

TABLE I

RATE CONSTANTS FOR THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH TOLUENE AT 25.0°

Solvent	Reactants, M: [$C_6H_5COCl\cdot AlCl_3$]	[C_6H_5COCl]	[$C_6H_5CH_3$]	Rate constant $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
TCB[a]	0.0942	0	0.0942	0.18
TCB	.0906	0	.276	.18
TCB	.275	0	.275	.30
TCB	.276	0.203	.277	.28
TCB	.274	0	.0992	.30
TCB	.642	0	.277	.50
DCB[b]	.0949	0	.289	.43
DCB	.293	0	.293	.49
DCB	.677	0	.289	.78
MC[c]	.0973	0	.289	.63
MC	.307	0	.307	.78
MC	.312	0.204	.312	.85
MC	.307	0	.682	.77

[a] 1,2,4-Trichlorobenzene. [b] *o*-Dichlorobenzene. [c] Methylene chloride.

The results show that the magnitude of the rate constants increase with the solvent in the order: 1,2,4-trichlorobenzene < *o*-dichlorobenzene < methylene chloride < ethylene chloride. However, the kinetic features of the acylation reaction appear to be the same in the four solvents. A change in the initial toluene concentration causes no change in the calculated second-order rate constants, whereas an increase in the initial concentration of the complex results in a moderate increase in the value of the rate constant. The addition of excess benzoyl chloride causes no significant change in the magnitude of the constant.

Benzoyl Bromide–Aluminum Bromide.—The insolubility of free aluminum chloride in these solvents made it necessary to utilize the soluble aluminum bromide in studies of the effect of excess metal halide. Solutions of aluminum bromide in 1,2,4-trichlorobenzene proved to be stable over periods of several weeks. Consequently, this solvent was adopted for the kinetic measurements. Benzoyl bromide was utilized as the acid halide to avoid the complication of halogen exchange between the metal halide and the acyl halide.

TABLE II

RATE CONSTANTS FOR THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH TOLUENE IN ETHYLENE DICHLORIDE

Temp., °C.	Reactants, M: [$C_6H_5COCl\cdot AlCl_3$]	[C_6H_5COCl]	[$C_6H_5CH_3$]	Rate constant $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
25.0	0.100	0	0.100	0.763
25.0	.100	0	.200	.777
25.0	.100	0	.300	.771
25.0	.100	0.100	.100	.776
25.0	.100	0.200	.100	.776
25.0	.150	0	.150	.849
25.0	.200	0	.100	.960
25.0	.200	0	.200	.965
25.0	.240	0	.240	1.01
25.0	.300	0	.100	1.08
25.0	.300	0	.300	1.09
0.0	.100	0	.100	0.0874
35.0	.100	0	.100	1.59

The experimental results are summarized in Table III.

TABLE III

RATE CONSTANTS FOR THE REACTION OF BENZOYL BROMIDE–ALUMINUM BROMIDE WITH TOLUENE AT 25.0° IN 1,2,4-TRICHLOROBENZENE

Reactants, M: [$C_6H_5COBr\cdot AlBr_3$]	[$C_6H_5CH_3$]	Rate constant $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
0.312	0.156	0.420
.311	.311	.423
.310	.617	.422
.0242	.311	.200
.0526	.311	.228
.105	.311	.268
.200	.309	.330
.309	.308	.387
.500	.311	.522
.504	.307	.538
.676	.309	.675
.774	.301	.782
1.025	.309	.895
1.024	.312	.925

The reaction of benzoyl bromide–aluminum bromide with toluene exhibits characteristics similar to those of the chloride reaction. For any initial concentration of the complex, the reaction appears to be clearly second order. Changes in the toluene concentration from 0.156 to 0.617 M have no significant effect on the rate constant. However an increase in the initial concentration of the complex produces an increase in the calculated second-order rate constant. The increase in the rate constant with increase in concentration of the complex is very similar for both the chloride and bromide (Fig. 1). The two reactions are quite similar in

rate. At the same concentration (0.3 M) in 1,2,4-trichlorobenzene, the benzoyl bromide–aluminum bromide complex reacts with toluene 20% faster then does the corresponding chloride complex.

The marked catalytic effect of aluminum halide present in excess over the concentration of the acid halide has been noted previously.[11–14] Olivier[12] reported that in the presence of excess aluminum bromide the data for individual experiments followed a second-order rate expression and the value of the second order rate constant varied with the concentration of free aluminum bromide. At relatively low aluminum bromide concentrations, we also observed second-order kinetics (Table III). However, at somewhat higher aluminum bromide concentration, the reactions appeared to be pseudo third order (Table IV).

TABLE IV

RATE DATA ILLUSTRATING THE DEPENDENCE OF THE KINETIC ORDER ON THE CONCENTRATION OF EXCESS ALUMINUM BROMIDE IN THE REACTION OF BENZOYL BROMIDE–ALUMINUM BROMIDE WITH TOLUENE IN 1,2,4-TRICHLOROBENZENE AT 25°

Excess $AlBr_3$ M	Time, min.	Reactants[a] [$C_6H_5COBr \cdot AlBr_3$] M	Rate constants: k_2,[b] l. mole^{-1} sec.$^{-1}$	Rate constants: k_3,[c] l.^{2} mole^{-2} sec.$^{-1}$
0.154	0	0.309		
	2.84	.230	.....	....
	8.15	.1578	0.00625	0.0303
	13.11	.1255	.00588	.0355
	23.48	.0839	.00603	.0493
	28.07	.0752	.00591	.0515
			Av. 0.00603	
0.309	0	0.309		
	1.90	.1637	.....	....
	3.64	.1242	0.0187	0.132
	5.10	.1093	.0159	.121
	6.76	.0955	.0150	.126
	8.30	.0848	.0148	.132
	9.84	.0788	.0138	.130
				Av. 0.128
0.617	0	0.309		
	0.84	.152		
	2.25	.0998	0.0407	0.337
	3.77	.0792	.0345	.326
	5.89	.0652	.0290	.318
	8.14	.0548	.0267	.328
	9.76	.0481	.0265	(.365)
				Av. 0.327

[a] $[C_6H_5CH_3]_0 = 0.309\ M$. [b] Rate $= k_2[a - x]^2$. [c] Rate $= k_3[a - x]^3$.

The rate constants for the kinetic studies with excess aluminum bromide are summarized in Table V. With initial concentrations of toluene and the addition compound of 0.3 M, the initial rate of reaction is increased about 100-fold by the presence of an additional mole of aluminum bromide ($AlBr_3$). The presence of two molar quantities of aluminum bromide increases the initial rate of reaction by a factor of approximately 500.

Discussion

Kinetics of the Benzoyl Halide–Aluminum Halide Reaction with Aromatics.—The present study confirms earlier reports that the reaction of benzoyl halide–aluminum halide is first order in each component, but that the second-order rate constants increase with increasing initial concentration of the acyl halide–metal halide addition compound.[11,14] The sole exception to this conclusion is provided by the recent data of Smeets and Verhulst[15] for the reaction in benzene at 35°.

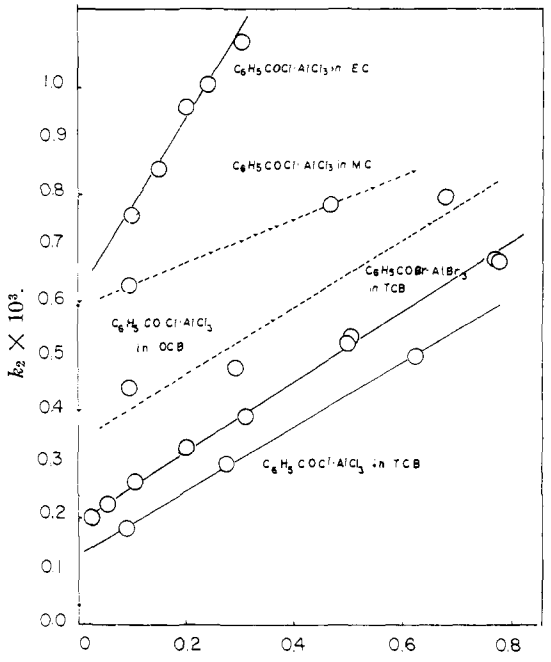

Fig. 1.—Change in the second-order rate constant with change in the initial concentration of the acid halide–aluminum halide complex.

TABLE V

RATE CONSTANTS FOR THE REACTION OF BENZOYL BROMIDE–ALUMINUM BROMIDE WITH TOLUENE IN THE PRESENCE OF EXCESS ALUMINUM BROMIDE IN 1,2,4-TRICHLOROBENZENE AT 25°

Reactants, M: [$AlBr_3$]	Reactants, M: [$C_6H_5COBr \cdot AlBr_3$]	Reactants, M: [$C_6H_5CH_3$]	Rate constants: $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$	Rate constants: $k_3 \times 10^3$, l.^{2} mole^{-2} sec.$^{-1}$
0	0.309	0.309	0.405	
0.154	.300	.300	6.05	
.309	.309	.309		128
.465	.311	.310		225
.617	.309	.309		327

These authors followed the reaction by sweeping out the evolved hydrogen chloride and titrating it, whereas we and Olivier[12] followed the reaction by determination of residual benzoyl halide. In spite of different analytical procedures for the acid halide, our kinetic results and conclusions are in excellent agreement with those of Olivier where they can be compared.

Unfortunately, Smeets and Verhulst failed to discuss this discrepancy between their results and those of earlier workers.[16] Until this discrepancy has been resolved, we shall proceed on the basis

(16) The Referee has pointed out that the kinetics may be influenced by the partial pressure of hydrogen chloride and this may be responsible for the difference in results.

indicated by the majority of the data that the rate constant for the reaction of the benzoyl halide–aluminum halide addition compound with simple aromatics in non-polar solvents increases generally with increasing initial concentration of the complex.

There is considerable evidence that the rate of the benzoylation reaction is quite sensitive to the polarity of the reaction medium. Thus the reaction rate increases moderately as the solvent is altered from 1,2,4-trichlorobenzene, to *o*-dichlorobenzene, to methylene chloride, to ethylene chloride, with a further large increase with benzoyl chloride (Table VI).

TABLE VI

COMPARISON OF RATES OF REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH TOLUENE AT 25.0°

Solvent	Rate constant,[a] $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$	Relative rate
1,2,4-Trichlorobenzene	0.18	1.0
o-Dichlorobenzene	.43	2.4
Methylene chloride	.63	3.5
Ethylene chloride	0.76	4.2
Benzoyl chloride	5.43	30

[a] Concentration of complex, 0.10 *M*.

On this basis the increase in rate with increase in the initial concentration of the benzoyl chloride–aluminum chloride, observed in the non-polar reaction media, might be the result of a solvent effect. These addition compounds are highly polar substances with high dipole moments.[17] Their presence in the non-polar solvents would be expected to modify significantly the polarity of the medium. The reaction products, $R_2CO.AlCl_3$, have similar dipolar properties. Olivier[12] demonstrated that the addition of benzophenone–aluminum bromide to a typical reaction mixture resulted in the same increase in the observed rate constant as an equivalent increase in the initial concentration of benzoyl bromide–aluminum bromide. Consequently, the polarity of the solvent should depend primarily on the initial concentration of the complex and would not be expected to change significantly as the reaction proceeds.

Benzoyl chloride itself is a highly polar reaction medium. In this solvent the rate of the benzoylation reaction is independent of the initial concentration of the complex.[9] Consequently, the experimental observations are consistent with a "salt effect" of the addition compounds in these non-polar solvents. However, it should be pointed out that alternate interpretations, such as a weak catalytic effect of the addition compounds, are also possible.

In spite of the difference in kinetics for the benzoylation reaction in benzoyl chloride and in these non-polar solvents, the actual substitution stage must be quite similar. This is indicated by the similarity in the entropies of activation for the two reactions (Table VII), the similarity in the toluene/benzene reactivity ratio[18] and the similarity in the isomer distribution.[18]

In previous publications we have considered the

(17) W. Nespital, *Z. physik. Chem.*, **B16**, 153 (1932).

(18) H. C. Brown and G. Marino, THIS JOURNAL, **81**, 3308 (1959).

TABLE VII

DERIVED DATA FOR THE BENZOYLATION OF BENZENE AND TOLUENE

Compound	Solvent	Energy of activation $E_{act.}$, kcal./mole	log A, sec.$^{-1}$	Enthalpy of activation $\Delta H^{\ddagger}$, kcal./mole	Entropy of activation $\Delta S^{\ddagger}$, e.u.
Benzene	BC[a]	15.8	7.28	15.1	−27.2
Toluene	BC[a]	13.3	7.49	12.6	−26.7
Toluene	EC[b]	13.9	7.08	13.3	−28.1

[a] Benzoyl chloride (ref. 9). [b] Ethylene chloride.

two mechanisms which appear possible for the benzoylation reaction,[9,10] a direct reaction of the aromatic with the addition complex or a prior ionization of the complex followed by reaction of the aromatic with the ion-pair intermediates.[19,20] The present data do not distinguish between these mechanisms.[21] A complete understanding of the aluminum chloride-catalyzed acylation mechanism requires a better understanding of the structures of the acyl chloride–aluminum chloride complexes[22,23] as well as information as to the extent and rate of ionization of these complexes in various reaction media.[24]

The reaction of benzoyl bromide–aluminum bromide with toluene appears to be essentially identical with the related reaction of the chlorine derivative. The kinetics are the same, the rate constants exhibit the same change with initial complex concentration, and the actual second-order rate constants differ by only a small factor (20%). Consequently, it is probable that both reactions proceed through identical paths.

In the presence of excess methyl bromide, dimeric aluminum bromide, Al_2Br_6, dissociates to form the 1:1 compound, $CH_3Br:AlBr_3$. In the presence of excess aluminum bromide, the 1:2 compound forms $CH_3Br:Al_2Br_6$.[25] Presumably the addition of excess aluminum bromide to the 1:1 benzoyl bromide–aluminum bromide complex results in its conversion to a 1:2 derivative, $C_6H_5COBr\cdot Al_2Br_6$.[12] The marked increase in reaction rate accompanying the introduction of excess aluminum bromide is readily accounted for in terms of the greater electrophilicity of the 1:2 complex, or in terms of its more extensive ionization.

The alteration in order from second, with minor amounts of excess aluminum bromide, to third with larger amounts, is more difficult to explain. Although it is possible to devise kinetic schemes which account for these changes in reaction order, these schemes must be considered highly speculative in the absence of direct knowledge of the molecular species present in the solutions. Conse-

(19) G. Baddeley and D. Voss, *J. Chem. Soc.*, 418 (1954).

(20) For a detailed review of these two mechanisms see P. H. Gore, *Chemistry & Industry*, 1385 (1954); *Chem. Revs.*, **55**, 229 (1955).

(21) Recently the preparation of several ionic acylonium fluoroborates, $RCO^+BF_4^-$, was described and their ready reaction with aromatics noted; G. Olah and S. Kuhn, *Ber.*, **89**, 866 (1956).

(22) N. N. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **21**, 1788 (1951).

(23) B. P. Susz and I. Cooke, *Helv. Chim. Acta*, **37**, 1273 (1954); I. Cooke, B. P. Susz and C. Herschmann, *ibid.*, **37**, 1280 (1954); B. P. Susz and J. J. Wuhrmann, *ibid.*, **40**, 971 (1957).

(24) J. L. Huston and C. E. Lang, *J. Inorg. Nucl. Chem.*, **4**, 30 (1957).

(25) H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6279 (1953).

quently, discussion of this phase of the investigation will be deferred.

In conclusion, it appears that the reaction of benzoyl chloride–aluminum chloride with toluene in 1,2,4-trichlorobenzene or ethylene chloride is relatively simple kinetically and closely related to the previously studied reactions of this complex in benzoyl chloride solution.[9] The simplicity of the experimental technique should facilitate the determination of the effects of substituents in the aromatic on the substitution rates. The variation in the rate constant with initial concentration represents a minor difficulty which should be circumvented readily either by comparing rate constants at infinite dilution or by comparing them at the same concentrations. The related simple kinetics observed for the corresponding reaction of benzoyl bromide–aluminum bromide with toluene in 1,2,4-trichlorobenzene supports the conclusion that this system should also prove applicable to a study of the effect of various metal halides on the rate, as well as the investigation of the influence of the structure of the acyl halide upon the reaction.[26]

Experimental Part

Materials.—The 1,2,4-trichlorobenzene was isolated from a mixture of isomers (Hooker Electrochemical Co.) by washing with fuming sulfuric acid, followed by water, drying over calcium sulfate, and then slowly fractionating the material through a column rated at 70 plates. *o*-Dichlorobenzene, methyl chloride and ethylene chloride were commercial products which were treated with fuming sulfuric acid, washed with water, and distilled in the same column. In all cases, only the central fractions of constant boiling points were used.

Benzoyl chloride was purified in the manner described previously.[9] Benzoyl bromide was twice distilled through the 70-plate column, packed with glass helices, under reduced pressure, with careful protection from air and moisture.

The preparation of pure colorless aluminum chloride[9] and aluminum bromide[27] has been described in previous publications in this series.

Preparation of Solutions.—Standard solutions of the complex, $C_6H_5COCl{\cdot}AlCl_3$, in the various solvents were prepared by adding equivalent amounts of benzoyl chloride and aluminum chloride to the appropriate solvent, with careful exclusion of moisture. A glass enclosed magnetic bar was added and the solution was stirred vigorously to facilitate the formation of the complex. Since the aluminum chloride dissolved relatively slowly, the solutions were usually warmed to facilitate the process. Although the solutions were originally colorless, warming frequently resulted in a slight yellowing. No further color change was visible following the addition of toluene. These slight colors appeared to be due to the presence of trace quantities of impurities. Since the rate constants proved to be readily reproducible and did not appear to be influenced by the presence or absence of these slight colors, we concluded that they had no significant effect upon the kinetics.

To test possible reaction with the solvent, a standard solution of benzoyl chloride–aluminum chloride in 1,2,4-trichlorobenzene was prepared. Analysis for benzoyl chloride indicated the presence of 98.3% of the calculated amount. After 48 hours at 25°, the solution was again analyzed. The concentration of benzoyl chloride was unchanged.

A solution of aluminum bromide in 1,2,4-trichlorobenzene was prepared and allowed to stand for several weeks. The solution remained clear, with no noticeable change. After hydrolysis, the organic material exhibited properties identical with those of the original solvent.

In reactions involving aluminum bromide, advantage was taken of its solubility by preparing standard solutions of both aluminum bromide and of benzoyl bromide in 1,2,4-trichlorobenzene and preparing the reaction solutions by mixing measured volumes of these two solutions with the solvent.

The special apparatus and techniques developed previously for handling benzoyl chloride solutions[9] were utilized.

Kinetic Measurements.—The reaction solutions were measured in the special storage flasks[9] and introduced into the reaction vessels. The latter were connected to a dry nitrogen supply and a small pressure was maintained in the system so that removal of the stopper automatically resulted in a flow of nitrogen through the narrow neck of the flask. After the solutions had reached temperature equilibrium with the bath (±0.03°), the reaction was initiated by adding the toluene.

Aliquots for analysis were withdrawn in the steam of nitrogen using fast delivery pipets which had been calibrated for delivery with the individual solvents. The aliquots were analyzed volumetrically for residual benzoyl chloride using the procedure previously developed for studying the rate in nitrobenzene solution.[7]

For the preliminary survey in the various solvents, we were content with a precision of ±5% (Table I). For the remaining study (Tables II and III) we sought a higher precision, ±2%. A typical study is summarized in Table VIII.

TABLE VIII

TYPICAL DATA FOR THE REACTION OF BENZOYL CHLORIDE–ALUMINUM CHLORIDE WITH TOLUENE IN ETHYLENE CHLORIDE SOLUTION AT 25.0

Time, min.	NaOH, ml.	Reaction,[a] %	$\frac{x}{a-x}$	Rate constant[b] $k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
0	8.82[c]			
2.00	8.75	0.79		
71.0	6.60	25.17	0.3363	0.789
170	4.90	44.44	0.7998	.784
248	4.12	53.28	1.1404	.766
285	3.75	57.48	1.3515	.790
362	3.26	66.04	1.7056	.785
452	2.85	67.69	2.0950	.772
532	2.55	71.09	2.4590	.770

[a] Initial concentrations: $[C_6H_5CH_3]$ 0.100 *M*; $[C_6H_5COCl{\cdot}AlCl_3]$ 0.100 *M*. [b] Graphical evaluation: k_2 0.779 × 10^{-3} l. mole^{-1} sec.$^{-1}$. [c] Calcd.

The precision attained is also indicated by the agreement between the rate constants in individual determinations: $[C_6H_5COCl{\cdot}AlCl_3]$, $[C_6H_5CH_3]$ 0.100 *M*, k_2 = 0.778, 0.741, 0.779, 0.755; $[C_6H_5COCl{\cdot}AlCl_3]$, $[C_6H_5CH_3]$ 0.200 *M*, k_2 = 0.952, 0.999, 0.947, 0.964; $[C_6H_5COCl{\cdot}AlCl_3]$, $[C_6H_5CH_3]$ 0.300 *M*, k_2 = 1.075, 1.100, 1.089. Average values for the rate constants are listed in Table II.

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(26) A study of the reaction rates exhibited by a number of substituted benzoyl chlorides has been completed by G. Marino and will be reported shortly.

(27) H. C. Brown and H. Jungk, THIS JOURNAL, **77**, 5579 (1955).