increased when it is introduced into an aromatic solvent, and the same may hold true for an N-succinimidyl radical. The effect of solvent on the isotope effect for chlorination was noted here also, the value obtained at 110° in toluene solution (1.47) being significantly larger than that obtained at 77° in carbon tetrachloride (1.30).

There is also a question as to whether the chlorination by sulfuryl chloride involves a chlorine radical or a $SO_2Cl\cdot$ radical.[18] If the latter were involved, and it had a significantly different reactivity difference for H and D than does the chlorine radical, this would be observed in the isotope effects of the two reactions. The reaction with N-chlorosuccinimide gives, within the experimental error, the same isotope effect as does the reaction with chlorine, and the chlorination by sulfuryl chloride gives a significantly larger isotope effect. This adds weight to the idea that another species than the chlorine radical is to at least a small extent involved in the hydrogen abstraction step for the latter reagent. It should be noted that in carbon tetrachloride solution only a small difference was found in the isotope effects for the reactions with chlorine and with sulfuryl chloride (Table III).

Acknowledgment.—We wish to thank the National Science Foundation for their support of this work, and the Atomic Energy Commission for assistance in obtaining certain equipment for the mass spectrometer. We also wish to thank Mr. B. J. Nist for his invaluable assistance in obtaining the mass spectra.

SEATTLE, WASHINGTON

(18) G. A. Russell and H. C. Brown, THIS JOURNAL, **77**, 4031 (1955).

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

Effect of Various Friedel–Crafts Catalysts on the Rates and Kinetics of the Reaction of Benzoyl Chloride with Aromatics[1,2]

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The metal chloride-catalyzed Friedel–Crafts acylation of aromatics in benzoyl chloride as solvent proceeds far faster with gallium chloride, ferric chloride and antimony pentachloride than does the corresponding reaction with aluminum chloride. On the other hand, the catalysis by stannic chloride, boron chloride and antimony trichloride is far smaller than that by aluminum chloride. The observed effects of the metal halides on the rate of the benzoylation reaction at 25° ($SbCl_5$, 1300; $FeCl_3$, 570; $GaCl_3$, 500; $AlCl_3$, 1; $SnCl_4$, 1/350; BCl_3, 1/1600; $SbCl_3$, very small) does not correspond to the relative strengths of these Lewis acids. Instead of the simple second-order kinetics exhibited by the aluminum chloride reaction, the fast reactions follow the alternative kinetic expression: rate $= (k_3/[MCl_n]_0)[MCl_n]^2[ArH]$. On the other hand, the slow reaction with stannic chloride and boron chloride appears to follow the alternative kinetic expression (similar to that previously observed with aluminum chloride): rate $= k_2[MCl_n][ArH]$. The similarity in the isomer distributions realized in the benzoylation of toluene argues for a common reaction intermediate, presumably the acylonium ion, $C_6H_5CO^+$, in the substitution stage. The difference in the reaction kinetics can be rationalized in terms of the role of the metal halide in ionizing the benzoyl chloride.

Aluminum chloride is by far the most commonly used Friedel–Crafts catalyst for the acylation of aromatics.[5] However, numerous other metal halides have been utilized as catalysts for this reaction.

Attempts have been made to ascertain the relative effectiveness of various catalysts in the acylation reaction by comparing the yields of ketones realized in these reactions.[6,7] Such methods can provide only rough qualitative information. The recent observation that the benzoylation of aromatics by aluminum chloride in benzoyl chloride proceeds by clean second-order kinetics[8] suggested that a kinetic approach might provide a more quantitative understanding of the effect of the metal halide on this reaction. Such information should be of value in guiding the selection of the most favorable catalyst in acylations and in furthering our understanding of the role of the metal halide catalyst in Friedel–Crafts reactions. For this reason we undertook a study of the rates and kinetics of the benzoylation reaction in benzoyl chloride solution utilizing the chlorides of antimony(III, V), gallium(III), iron(III), boron(III) and tin(IV).

We had anticipated that all of these metal halides would exhibit the simple second-order kinetics of the aluminum chloride reaction

$$\text{rate} = k_2[AlCl_3][ArH] \qquad (1)$$
$$\text{or rate} = k_2[C_6H_5COCl\cdot AlCl_3][ArH]$$

with the magnitudes of the rate constants reflecting the strengths of the metal halides as Lewis acids. However, we observed markedly different kinetics for some of the metal halides studied, with some of the catalytic activities being far greater than that of aluminum chloride, presumably the strongest Lewis acid in the group.

Results

Gallium Chloride.—Gallium halides have received only limited attention as Friedel–Crafts catalysts, probably because of the cost and scarcity

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(1) The Catalytic Halides. XXII.

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

(3) Department of Chemistry, University of California, Berkeley, California.

(4) Research assistant on a project supported by the Atomic Energy Commission, 1953–1954; National Science Foundation Predoctoral Fellow, 1954–1955.

(5) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941.

(6) N. O. Calloway, *Chem. Revs.*, **17**, 327 (1935).

(7) O. C. Dermer, D. M. Wilson, F. M. Johnson and V. H. Dermer, THIS JOURNAL, **63**, 2881 (1941); O. C. Dermer and R. A. Billmeier, *ibid.*, **64**, 464 (1942); O. C. Dermer, P. T. Mori and S. Suguitan, *Proc. Oklahoma Akad. Sci.*, **29**, 74 (1948).

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

of the element. Ulich and Heyne utilized gallium chloride for both alkylation and acylation, but reported the formation of an unidentified yellow product in the acylation of benzene.[9]

The high solubility of gallium chloride in alkyl chlorides proved advantageous in studying the addition compounds of these halides with Friedel–Crafts catalysts.[10] Moreover, gallium bromide is an effective alkylation catalyst[11] which avoids many of the complicating side-reactions accompanying the use of the more powerful catalyst, aluminum bromide.[12] Accordingly, it appeared desirable to include gallium chloride in this study.

Gallium chloride dissolves in benzoyl chloride to form a colorless solution.[13,14] The solution remains colorless after the addition of toluene. A slight yellow tinge was observed only after 20 hours, long after the reaction was complete.

In a preliminary survey of the reaction, a reaction mixture was made up, 0.382 *M* in $GaCl_3$ and 0.362 *M* in toluene. Samples were removed in 2.7, 7, 370 and 1240 min., and analyzed for the methylbenzophenone product. To our surprise the reaction was complete in the first sample. The results are summarized in Table I.

TABLE I

REACTION OF BENZOYL CHLORIDE–GALLIUM CHLORIDE WITH TOLUENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Product, g./4.92 ml. ($C_6H_5COC_6H_4CH_3$)	Reaction, %
2.7	0.3547	100.5
7.0	.3551	100.6
370	.3548	100.5
1243	.3553	100.7[a]

[a] Reaction product tinged yellow.

Under identical conditions, the corresponding reaction involving aluminum chloride exhibits a half-life of 9.5 min., whereas the half-life of the present reaction is considerably smaller than 2.7 min., probably less than a small fraction of a minute.

With the aromatic present in limiting quantity (Table I), the reaction proceeds rapidly to the formation of the monoacylated derivative and then stops completely.

$$C_6H_5COCl\cdot GaCl_3 + ArH \longrightarrow C_6H_5COAr\cdot GaCl_3 + HCl$$

With excess aromatic the reaction proceeds slowly following the initial rapid formation of one mole of ketone per mole of catalyst present. The results are summarized in Table II.

Previously, it was observed that with aluminum chloride as catalyst the benzoylation reaction proceeds at a very slow rate following the initial rapid formation of one mole of ketone per mole of catalyst.[8] In the case of gallium chloride this subsequent reaction is far faster. Greenwood and Wade[14] report that they obtained 27% benzophenone from a refluxed reaction mixture of excess benzene, benzoyl chloride and 10 mole per cent. of gallium chloride.

TABLE II

REACTION OF BENZOYL CHLORIDE–GALLIUM CHLORIDE WITH EXCESS *p*-XYLENE AND TOLUENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Reactants, *M*			Product, *M*	Moles ketone / Mole catalyst
	$GaCl_3$	Toluene	*p*-Xylene	C_6H_5COAr	
0	0.285	0.995		0	
250				0.411	1.44
1360				.503	1.77
0	0.371		0.584		
3.4				.429	1.15
9.9				.450	1.28
120.6				.518	1.39
336.5				.565	1.52

The reactions with toluene and *p*-xylene are too fast to be measured by our present methods. The reactions with benzene are also quite fast, with a half-life of about 3 min. (Table III). Although a rough kinetic study was possible with benzene, we chose to carry out a detailed study with a less reactive compound, chlorobenzene, so that data could be obtained for the initial phases of the reaction, thus avoiding the possible complication of the subsequent reaction discussed previously.

TABLE III

KINETIC DATA FOR THE REACTION OF BENZOYL CHLORIDE–GALLIUM CHLORIDE WITH BENZENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Reactants,[a] *M* $a - x$	Product, *M* x
0	0.310	0.000
1.33	.234	.076
3.64	.166	.144
10.1	.098	.212
30.2	.053	.257
81.8	.028	.282[b]

[a] $[GaCl_3] = [C_6H_6] = 0.310$ *M*. 91% reaction.

With this aromatic the reaction proceeded at a convenient rate for measurement, and satisfactory rate data, easily and precisely reproducible, were readily obtainable. However, the kinetics exhibited unexpected features. On the basis of the stoichiometric reaction, the calculated rate constants decrease as the reaction proceeds (Fig. 1). On the other hand, third-order rate constants based upon the expression

$$\text{rate} = k_3[GaCl_3]^2[C_6H_5Cl] \qquad (2)$$

exhibit a satisfactory constancy (Table IV, Fig. 2).

The third-order rate constants calculated from the integrated forms of expression 2 vary with the initial concentration of gallium chloride. However, the product of the third-order constant and the initial concentration of gallium chloride is constant. The reaction is first order in chlorobenzene. These results suggest that the complete rate expression is

$$\text{rate} = \frac{k_3}{[GaCl_3]_0}[GaCl_3]^2[C_6H_5Cl] \qquad (3)$$

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(9) H. Ulich and G. Heyne, *Z. Elektrochem.*, **41**, 509 (1935).

(10) H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953); R. Wong and H. C. Brown, *J. Inorg. Nucl. Chem.*, **1**, 402 (1955).

(11) C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 6245, 6249 (1956).

(12) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956).

(13) The isolation of the 1:1 addition compound, $C_6H_5COCl\cdot GaCl_3$, analogous to the aluminum derivative, $C_6H_5COCl\cdot AlCl_3$, has been reported; H. Ulich and G. Heyne, *Z. physik. Chem.*, **B49**, 284 (1941).

(14) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956). Contrary to our observations, the originally colorless solutions obtained by these investigators tended to discolor through pale straw to green.

Considering only the initial phases of the reactions it is impossible to differentiate between expression 3 or an expression similar to 1 as being the correct kinetic equation. We considered the possibility that the deviation from the second-order plot was due to the presence of some impurity which caused the rate to decrease in the latter stages. However, careful purification of the reagents failed to eliminate the observed decrease in rate. Moreover, the data were highly reproducible in various runs with different batches of reagents. We were therefore forced to consider the possibility that the observed data were the result of a kinetic order other than the simple second order we had anticipated. Several other equations were investigated but we were able to correlate the data only by equations 2 and 3.

All of the kinetic data are reproduced with considerable precision by the rate expression 3. Because of the peculiar form of expression[3] it is difficult to eliminate entirely the possibility that the reaction follows the simple second-order expression exhibited by aluminum chloride, with the decrease in the rate constants (Fig. 1) arising from secondary causes. However, the precision with which rate expression 3 correlates all of our rate measurements for gallium chloride, as well as the related data for ferric chloride and antimony pentachloride, provides a powerful argument for its applicability to these acylation reactions.

The rate data are summarized in Table V.

Rate constants for the reactions were determined at several temperatures and the enthalpies and entropies of activation calculated (Table VI).

Ferric Chloride.—Ferric chloride forms 1:1 addition compounds[15] with both benzoyl chloride and benzophenone, $C_6H_5COCl{\cdot}FeCl_3$ and $(C_6H_5)_2CO{\cdot}FeCl_3$, related to the corresponding addition compounds of aluminum chloride. Ferric chloride has also received wide application as a Friedel–Crafts acylation catalyst, especially where a relatively mild catalyst was desired.

Again the results were unexpected in that ferric chloride proved to be an exceedingly powerful catalyst for the benzoylation reaction. The results were quite similar to those previously observed with gallium chloride. With the toluene present in limiting quantity, one mole of ketone per mole of ferric chloride was formed very rapidly. With excess toluene, the initially fast reaction leading to the formation of one mole of ketone per mole of metal halide was followed by a slower but appreciable further acylation of the excess aromatic. These results are summarized in Table VII.

Just as in the case of gallium chloride, individual experiments exhibit third-order kinetics, with the value of the third-order rate constant being inversely proportional to the initial concentration of the ferric chloride. The third-order plots fell off somewhat, presumably due to the difficulty of preparing pure ferric chloride. The results are summarized in Table VIII.

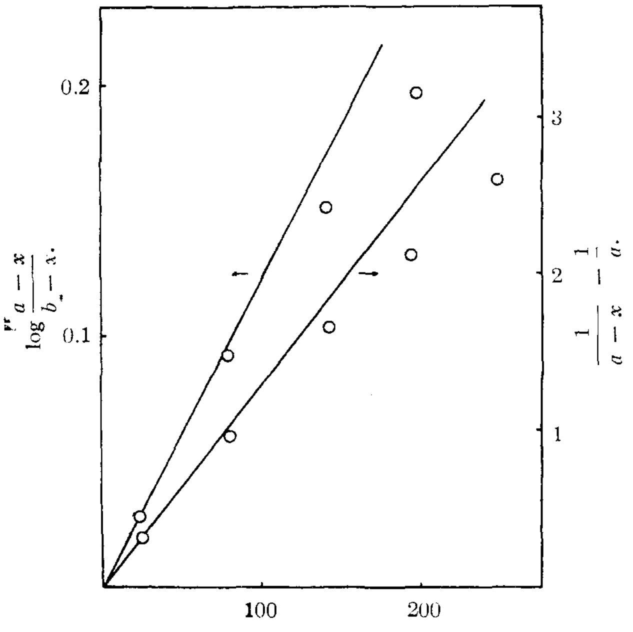

Fig. 1.—Second-order plots of the kinetic data for the gallium chloride-catalyzed benzoylation of chlorobenzene.

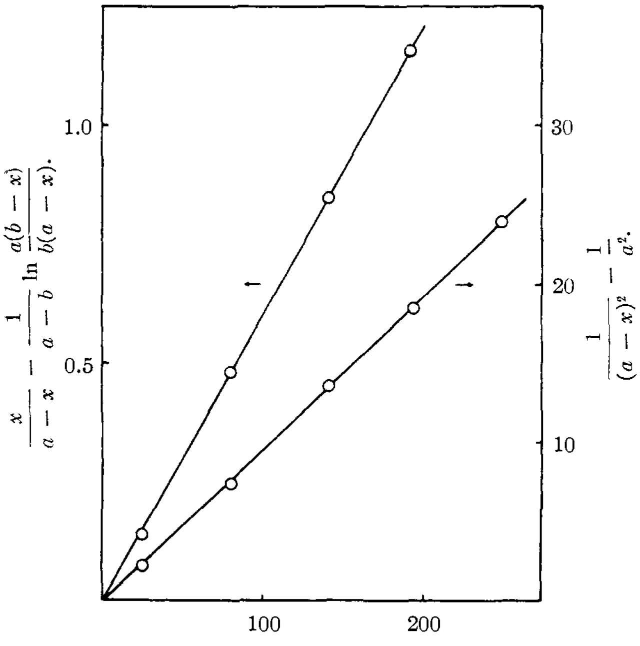

Fig. 2.—Third-order plots of the kinetic data for the gallium chloride-catalyzed benzoylation of chlorobenzene.

It is probable that the complete kinetic expression is identical with that involving gallium chloride.

$$\text{rate} = \frac{k_3}{[FeCl_3]_0}[FeCl_3]^2[C_6H_5Cl] \qquad (4)$$

Antimony Pentachloride.—Antimony pentachloride reacts with benzoyl chloride to form $C_6H_5COCl{\cdot}SbCl_5$[16] which has been reported to be

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(15) M. Necki, *Ber.*, **30**, 1766 (1897); J. Böeseken, *Rec. trav. chim.*, **22**, 215 (1903).

(16) H. Meerwein and H. Maier-Huser, *J. prakt. Chem.*, **134**, 51 (1932).

TABLE IV

TYPICAL KINETIC DATA FOR THE REACTION OF BENZOYL CHLORIDE-GALLIUM CHLORIDE WITH CHLOROBENZENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Reactants,[a] M $a - x$	Product, M x	Rate constant $k_2 \times 10^2$, l. mole^{-1} min.$^{-1}$	Rate constant $k_3 \times 10^3$, l.^{2} mole^{-2} min.$^{-1}$
0	0.3028	0.0000		
25.2	.2757	.0268		
80.5	.2333	.0692	1.18	4.74
141.9	.2016	.1009	1.14	4.88
195.0	.1839	.1186	1.07	4.83
248.5	.1694	.1331[b]	1.02	4.88

[a] $[GaCl_3] = [C_6H_5Cl] = 0.3028$ M. [b] 44% reaction.

TABLE V

VARIATION OF THE RATE CONSTANTS AT 25° WITH THE INITIAL GALLIUM CHLORIDE CONCENTRATION

Reactants, M GaCl$_3$	Reactants, M C$_6$H$_5$Cl	Rate constants $k_3 \times 10^2$, l.^{2} mole^{-2} min.$^{-1}$	Rate constants $k_3 \times 10^2$ [GaCl$_3$]$_0$, l. mole^{-1} min.$^{-1}$
0.1014	0.305	16.1	1.63
.202	.304	7.21	1.45
.302	.303	4.87	1.47
.510	.305	2.93	1.49
.301	.152	4.92	1.48

TABLE VI

VARIATION IN RATE CONSTANTS WITH TEMPERATURE AND DERIVED DATA FOR THE GALLIUM CHLORIDE-CATALYZED BENZOYLATION OF CHLOROBENZENE

	Temp., °C. 25.0	Temp., °C. 39.9	Temp., °C. 52.4
Rate constant, $k_3[GaCl_3]_0$	0.0147	0.0487	0.1297
Activation energy, E_{act}	15.4 kcal./mole		
Log A	7.68		
Enthalpy of activation, $\Delta H^{\ddagger}$	14.8 kcal./mole		
Entropy of activation, $\Delta S^{\ddagger}$	−25.4 e.u.		

TABLE VII

REACTION OF BENZOYL CHLORIDE-FERRIC CHLORIDE WITH TOLUENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Reactants, M FeCl$_3$	Reactants, M Toluene	Product, M C$_6$H$_5$COC$_6$H$_4$CH$_3$	Moles ketone / Mole catalyst
0	0.509	0.514	0	
3.5			0.500	0.98
37.8			.502	.99
3380			.512	1.01
0	0.243	1.05	0	
4.2			0.283	1.17
30.7			.317	1.31
158			.347	1.43
3360			.450	1.85

TABLE VIII

RATE DATA FOR THE FERRIC CHLORIDE-CATALYZED BENZOYLATION OF CHLOROBENZENE AT 25°

Reactants, M FeCl$_3$	Reactants, M C$_6$H$_5$Cl	Rate constants $k_3 \times 10^2$, l.^{2} mole^{-2} min.$^{-1}$	Rate constants $k_3 \times 10^2$ [FeCl$_3$]$_0$, l. mole^{-1} mole^{-1}
0.278	0.278	6.5	1.8
0.454	0.454	3.5	1.6

ionized in sulfur dioxide solution.[17] With benzophenone the 2:1 compound, $(C_6H_5)_2CO{\cdot}2SbCl_5$, has been described.[18]

Upon addition of small amounts of antimony pentachloride to benzoyl chloride, a clear, yellow-orange solution is obtained. With further addition of the metal halide, a copious yellow precipitate forms, presumably the 1:1 addition compound, which possesses only moderate solubility in benzoyl chloride. Since our procedure for following the kinetics loses precision at low concentrations of the reactants, we were unable to vary the initial concentration of the antimony pentachloride over a wide range.

However, in every respect the antimony pentachloride catalyzed reaction resembles the corresponding reactions catalyzed by gallium chloride and ferric chloride. The reactions with benzene and toluene are exceedingly fast, far too fast to follow by our procedure. The reaction with chlorobenzene could be followed and the reaction follows third-order kinetics closely (Table IX).

TABLE IX

TYPICAL KINETIC DATA FOR THE REACTION OF BENZOYL CHLORIDE-ANTIMONY PENTACHLORIDE WITH CHLOROBENZENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Time, min.	Reactants,[a] M $a - x$	Product, M x	Rate constant $k_2 \times 10^2$, l. mole^{-1} min.$^{-1}$	Rate constant $k_3 \times 10^2$, l.^{2} mole^{-2} min.$^{-1}$
0	0.208	0.0000		
4.7	.201	.0072	3.8	18.0
20.7	.182	.0259	3.3	17.4
80.5	.138	.0703	3.04	18.3
179	.098	.1099[b]	2.58	18.4

[a] $[SbCl_5] = [C_6H_5Cl] = 0.208$ M. [b] 53% reaction.

The similarity in the characteristics of the reactions to those of the gallium chloride and ferric chloride reactions lead to the conclusion that the data should be handled similarly (Table X) (5).

$$\text{rate} = \frac{k_3}{[SbCl_5]_0}[SbCl_5]^2[C_6H_5Cl] \qquad (5)$$

TABLE X

RATE DATA FOR THE ANTIMONY PENTACHLORIDE-CATALYZED BENZOYLATION OF CHLOROBENZENE AT 25°

Reactants, M SbCl$_5$	Reactants, M C$_6$H$_5$Cl	Rate constants $k_3 \times 10^2$, l.^{2} mole^{-2} min.$^{-1}$	Rate constants $k_3 \times 10^2[SbCl_5]_0$, l. mole^{-1} min.$^{-1}$
0.181	0.181	21.9	3.94
0.208	0.208	18.3	3.79

Antimony Trichloride.—The reaction of benzoyl chloride in the presence of antimony trichloride with various aromatics was studied by Menschutkin.[19] He observed that the reaction is far slower than the corresponding reaction with aluminum chloride. At 150° the reaction proceeded at a reasonable rate and Menschutkin reported that the reaction was first order in aromatic, first order in benzoyl chloride and pseudo second order in the antimony chloride (6).

$$\text{rate} = k_4[SbCl_3]_0{}^2[C_6H_5COCl][ArH] \qquad (6)$$

We attempted to utilize antimony trichloride as a catalyst in benzoyl chloride as a solvent. However, after 4 days at 25°, the yield of product was only 0.2% and we concluded that the reaction was too slow for measurement.

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(17) F. Seel and H. Bauer, *Z. Naturforsch.*, **2b**, 397 (1947).

(18) K. H. Meyer, *Ber.*, **41**, 2568 (1908).

(19) B. N. Menschutkin, *J. Russ. Phys. Chem. Soc.*, **45**, 1710 (1913); *C. A.*, **8**, 910 (1914); *J. Chem. Soc. Abst.*, **106**, 188 (1914).

Stannic Chloride.—Stannic chloride is frequently utilized as a Friedel–Crafts catalyst for the acylation of highly reactive aromatic nuclei.[20] Pfeiffer was unable to isolate any addition compound between benzoyl chloride and stannic chloride at temperatures as low as 0°.[21] Although Meyer was unable to isolate any addition compound between stannic chloride and benzophenone,[22] Pfeiffer later described the product $[(C_6H_5)_2CO]_2{\cdot}SnCl_4$.[23]

Numerous addition compounds of organic bases with stannic chloride have now been described.[24,25] Derivatives of stannic chloride with both one and two molecules of base have been prepared, $B{\cdot}SnCl_4$ and $B_2{\cdot}SnCl_4$.

Stannic chloride dissolves in benzoyl chloride to form a colorless solution which shows no apparent change with time. Upon addition of toluene, the solution turns a light yellow-green or light orange immediately, and then slowly turns green. Benzoylation of the toluene proceeds at a relatively slow rate. The reaction product was isolated and the infrared spectrum was examined. Although the peaks were less well defined than for the product of the aluminum chloride reaction, the spectra were sufficiently similar to justify the conclusion that the methylbenzophenones were the major product of the reaction. Consequently, a kinetic study was undertaken. For a single experiment the reaction is first order in the concentration of toluene

$$\text{rate} = k_1[C_6H_5CH_3]$$

The rate constants calculated on this basis exhibit a satisfactory constancy, whereas constants calculated on the basis of assumed second-order kinetics drift considerably (Table XI).

TABLE XI

TYPICAL KINETIC DATA FOR THE STANNIC CHLORIDE-CATALYZED REACTION OF BENZOYL CHLORIDE WITH TOLUENE IN BENZOYL CHLORIDE SOLUTION AT 25°

	Reactants, M			Rate constant	
Time, min.	$SnCl_4$ $a - x$	Toluene $b - x$	Product, M x	$k_2 \times 10^4$, l. mole^{-1} min.$^{-1}$	$k_1 \times 10^4$, min.$^{-1}$
0	0.398	0.935	0.0000		
51	.379	.916	.0195		
289	.309	.846	.0887	9.4	3.45
667	.209	.746	.1894	12.1	3.34
992	.149	.686	.2492	13.6	3.36
1224	.088	.625	.310	16.6	3.29

Variation of the initial stannic chloride concentration revealed that the first-order rate constant varied directly with the stannic chloride concentration. It was concluded that the reaction followed the kinetic expression

$$\text{rate} = k_2[SnCl_4]_0[C_6H_5CH_3] \quad (7)$$

The rate data are summarized in Table XII.

TABLE XII

RATE DATA FOR THE STANNIC CHLORIDE-CATALYZED BENZOYLATION OF TOLUENE AT 25°

Reactants, M			Rate constants		
$SnCl_4$	$C_6H_5CH_3$	C_6H_5-COlC[a]	$k_1 \times 10^4$, min.$^{-1}$	k_2[b] $\times 10^4$, l. mole^{-1} min.$^{-1}$	k_3[c] $\times 10^4$, l.^{2} mole^{-2} min.$^{-1}$
0.199	0.405	8.03	1.97	9.9	1.23
.396	.396	7.85	3.67	9.27	1.18
.882	.391	7.36	6.67	7.57	1.03
.337	.591	7.73	3.14	9.32	1.21
.399	.207	8.02	4.06	10.2	1.27
.398	.935	7.36	3.34	8.39	1.14

[a] Solvent. [b] $k_2 = k_1/[SnCl_4]_0$. [c] $k_3 = k_1/[SnCl_4]_0[C_6H_5COCl]$.

These kinetics indicate that stannic chloride is not tied up by the ketone formed in the initial stages of the reaction, as is the case with aluminum chloride and the other powerful catalysts examined in this study. Although Pfeiffer reported isolating the addition compound, $[(C_6H_5)_2CO]{\cdot}_2SnCl_4$, it may be that this compound is stable only in the crystalline state, and exists largely dissociated in dilute benzoyl chloride solution.

At 25° the reaction rate falls off after one mole of ketone is formed for each mole of catalyst. However, at 90° a reaction mixture 0.382 M in stannic chloride and 1.28 M in toluene yielded 2.3 moles of crude ketone per mole of catalyst. These observations suggest that the ketone–stannic chloride addition compound must be highly dissociated in dilute benzoyl chloride solution, especially at elevated temperatures, but with increasing concentration of the ketone combination occurs to reduce the reaction rate. On this basis a change would be anticipated in the latter part of the reaction to the kinetic expression

$$\text{rate} = k_2[SnCl_4][C_6H_5CH_3] \quad (7)$$

In the case of the other metal halides whose kinetics were examined, stable addition compounds of benzoyl chloride with the metal halide are known to exist. Consequently, the metal halides must exist in benzoyl chloride solution as the stable 1:1 addition compounds. Replacement of the metal halide terms in the kinetic expressions 1, 3, 4 and 5 by terms involving the corresponding $C_6H_5COCl{\cdot}MX_n$ addition compounds, would not alter the rate constants based on these expressions.

In the case of stannic chloride, such stable addition compounds have not been demonstrated. Indeed, a mixture of stannic chloride in benzoyl chloride fumes on exposure to air and behaves as a simple solution. Consequently, it is probable that the concentration of benzoyl chloride should appear in the rate expression independent of the stannic chloride term (8, 8′)

$$(\text{initial})\ \text{rate} = k_3[SnCl_4]_0[C_6H_5COCl][ArH] \quad (8)$$

$$\text{rate} = k_3[SnCl_4][C_6H_5COCl][ArH] \quad (8')$$

Third-order rate constants calculated with the aid of equation 8 are listed in Table XII. The agreement between these constants is slightly better than for the second-order rate constants.

Rate constants for the reaction were measured at three temperatures and the values used to determine the enthalpies and entropies of activation (Table XIII).

The observed entropy of activation for the stannic chloride catalyzed reaction, −48 e.u., appears at first sight to be abnormal for reactions of this type.

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[20] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., Second Edition, 1950, p. 579.

[21] P. Pfeiffer, *Ann.*, **376**, 385 (1910).

[22] K. H. Meyer, *Ber.*, **43**, 157 (1910).

[23] P. Pfeiffer, *Ann.*, **383**, 92 (1911).

[24] For a review of the literature prior to 1927, see P. Pfeiffer, "Organische Molekulverbindungen," Ferdinand Enke, Stuttgart, 1927.

[25] A. W. Laubengayer and W. C. Smith, THIS JOURNAL, **76**, 5985 (1954).

TABLE XIII

VARIATION IN RATE CONSTANTS WITH TEMPERATURE AND DERIVED DATA FOR THE STANNIC CHLORIDE-CATALYZED BENZOYLATION OF TOLUENE

Temp., °C.	Reagents, *M* $SnCl_4$	$C_6H_5CH_3$	C_6H_5COCl	$k_2{}^a \times 10^4$, l.^{2} mole^{-2} min.$^{-1}$
25.0	0.199	0.405	8.03	1.23
39.9	.1496	.398	8.10	2.95
49.9	.296	.587	7.77	4.82

Activation energy, E_{act} 10.9 kcal./mole
Log A 2.30
Enthalpy of activation, $\Delta H^{\ddagger}$ 10.3 kcal./mole
Entropy of activation, $\Delta S^{\ddagger}$ −48.0 e.u.

[a] Calculated using equation 8.

For example, for the reaction with toluene using aluminum chloride as catalyst, $\Delta S^{\ddagger} = -27$ e.u.[8] We have postulated that aluminum chloride is firmly bound to benzoyl chloride while stannic chloride exists essentially uncomplexed and that it is necessary for the catalyst and benzoyl halide to be brought together for reaction to occur. If this is correct, then it is reasonable to expect a difference of about 20–25 e.u. for the two reactions provided the basic mechanisms are identical. This difference is due to a decrease in the entropy accompanying complex formation between benzoyl chloride and stannic chloride during the course of the reaction.

Similarly, it is to be expected that the measured heat of activation should be low because of the reaction between the acid chloride and stannic chloride. The observed values for the reactions with toluene are 10.3 kcal./mole and 12.6 kcal./mole utilizing stannic chloride and aluminum chloride[8] respectively as catalysts.

Boron Chloride.—Boron chloride does not react with benzoyl chloride,[14] although the related derivative, $CH_3COCl \cdot BCl_3$, exists at low temperatures,[14,16] The strength of boron chloride as an acid is such[26] that one might predict the existence of the addition compound, $(C_6H_5)_2CO \cdot BCl_3$. Since boron chloride is readily lost from its simple solution in benzoyl chloride, the kinetic study was carried out in a closed system, opened only for brief intervals to remove aliquots.

The reaction was exceedingly slow, so an extensive kinetic study was not possible. However, the data for the initial reaction could be interpreted in terms of the expression

$$\text{rate} = k_2[BCl_3][C_6H_5CH_3) \qquad (9)$$

The data are summarized in Table XIV.

TABLE XIV

RATE DATA FOR THE BORON CHLORIDE-CATALYZED BENZOYLATION OF TOLUENE AT 25°

Reactants, *M* BCl_3	Toluene	Rate constant $k_2 \times 10^4$, l. mole^{-1} min.$^{-1}$
0.384	0.384	2.1
0.385	1.070	1.7

The behavior of this reaction is similar to that using stannic chloride as catalyst. The catalysts do not appear to form stable compounds with benzoyl chloride and the reactions proceed slowly. Therefore, the concentration of benzoyl chloride probably should be included in the rate expression with boron trichloride as well as with stannic chloride.

It was reported previously that boron chloride does not catalyze the reaction between acetyl chloride and toluene at 100°.[7] Possibly at this temperature the boron chloride escaped from the reaction vessel. However, Greenwood and Wade recently have reported the formation of a trace of 4-methylbenzophenone, in the boron chloride catalyzed reaction of benzoyl chloride with toluene, after 10 weeks at room temperature.[14]

Isomer Distribution.—It appeared that the isomer distribution realized in the benzoylation of toluene might contribute to an understanding of the reaction mechanism. Accordingly, toluene was benzoylated in benzoyl chloride solution at 25° using each of the metal halides as catalysts. Emphasis was placed on the analysis for the *ortho* isomer. The *meta* isomer was present in much smaller amounts, approximately 1.9 ± 0.5%, and a precise analysis for this component, such as that reported previously for the aluminum chloride reaction,[8] would have required an extensive study. The results are summarized in Table XV.

TABLE XV

ISOMER DISTRIBUTION IN THE METAL CHLORIDE-CATALYZED BENZOYLATION OF TOLUENE IN BENZOYL CHLORIDE SOLUTION AT 25°

Catalyst	Methylbenzophenones, % *Ortho*	*Meta* and *para*[a]
Aluminum chloride	9.3[b]	90.7
Gallium chloride	9.6	90.4
Ferric chloride	8.9	91.1
Antimony pentachloride	9.2	90.8
Stannic chloride	8.6[c]	
Boron chloride	7-8[c]	

[a] *Meta* and *para* content estimated by difference assuming 100% purity of product. *Meta* content from spectra estimated to be 1.9 ± 0.5%. [b] Product contains 9.3% *o*- 1.45% *m*- and 89.3% *p*-methylbenzophenones (ref. 8.). [c] Product contained small quantities of impurities.

Discussion

The experimental results on the kinetics and the relative rates of reaction using the various metal halides in the benzoylation reaction are summarized in Table XVI.

The effectiveness of the catalysts as measured by the relative rates of reaction varies over a factor of more than 10^6. Inclusion of data for the less reactive catalyst, antimony trichloride, would considerably extend the range. The relative effectiveness of the various catalysts may vary when benzoyl chloride is not used as solvent since its concentration may affect the rates of some of the reactions.

It had been anticipated that the various metal halides would initiate a simple second-order reaction similar to that observed in the case of aluminum chloride, with the relative rates reflecting the relative strengths of the Lewis acids.

In the case of aluminum chloride, stannic chloride and boron chloride this expectation appears to have been realized. At least all of these benzoylation reactions involve the metal chloride to the first power with the rates corresponding to the much

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(26) H. C. Brown and R. R. Holmes, THIS JOURNAL, 78, 2173 (1956).

TABLE XVI

RATE DATA AND RELATIVE RATES FOR THE METAL CHLORIDE-CATALYZED BENZOYLATION OF AROMATICS IN BENZOYL CHLORIDE SOLUTION AT 25°

Catalyst	Kinetic expression	Rate constants at 25°, l. mole^{-1} min.$^{-1}$ Toluene	Chlorobenzene	Relative initial rates	Enthalpy of activation ΔH^*, kcal./mole	Entropy of activation ΔS^*, e.u.
Antimony pentachloride	5		0.0386	1300		
Ferric chloride	4		.017	570		
Gallium chloride	3		.0148	500	14.8^d	−25.4
Aluminum chloride	1	0.326	$(3.4 \times 10^{-5})^b$	1.00	12.6^{c,e}	−26.7
Stannic chloride	7	9.3×10^{-4}		1/350	10.3^c	−48.0
Boron chloride	9	2.1×10^{-4}		1/1600		

[a] Rate equation used to calculate the rate constant. [b] Calculated from the rate constant at 70° (ref. 8). [c] Toluene. [d] Chlorobenzene. [e] The values for the benzene reaction are $\Delta H^* = 15.1$ kcal./mole, $\Delta S^* = -27.2$ e.u.

higher acid strength of aluminum chloride as compared to stannic and boron chlorides.

$$\text{rate} = k_2[\text{MCl}_n][\text{ArH}]$$
$$\text{AlCl}_3 > \text{SnCl}_4,\ \text{BCl}_3$$

The aluminum chloride-catalyzed reaction involves the stable 1:1 addition compound, $C_6H_5COCl{\cdot}AlCl_3$,

$$\text{rate} = k_2[\text{C}_6\text{H}_5\text{COCl}{\cdot}\text{AlCl}_3][\text{ArH}]$$

whereas the stannic chloride (and possibly the boron chloride) reaction apparently proceeds through separate stannic chloride and benzoyl chloride molecules.

$$\text{rate} = k_3[\text{SnCl}_4][\text{C}_6\text{H}_5\text{COCl}][\text{ArH}]$$

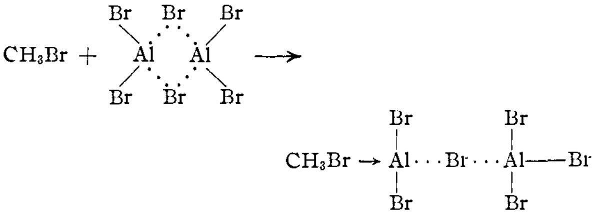
However, this is considered to be merely a minor modification which is reasonable in terms of the lower acid strength of the Lewis acid.

The marked change in kinetics and the fast rates exhibited by antimony pentachloride, ferric chloride, and gallium chloride are quite unexpected. These reactions possess the common feature that they involve a squared term in the metal halide, together with an inhibition term in the initial concentration of the metal halide. Since these metal chlorides are known to form stable 1:1 compounds with benzoyl chloride, the complete kinetic expression must be

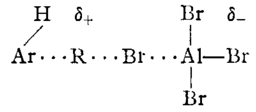
$$\text{rate} = \frac{k}{[\text{C}_6\text{H}_5\text{COCl}{\cdot}\text{MCl}_n]_0}[\text{C}_6\text{H}_5\text{COCl}{\cdot}\text{MCl}_n]^2[\text{ArH}]$$

There is growing evidence that weak organic donors can react with Friedel–Crafts catalysts to form both 1:1 or 1:2 addition compounds. For example, methyl chloride forms both $CH_3Cl{:}GaCl_3$ and $CH_3Cl{:}Ga_2Cl_6$,[27] and benzoyl bromide forms both derivatives, $C_6H_5COBr{\cdot}AlBr_3$ and $C_6H_5COBr{\cdot}Al_2Br_6$.[28] The phenomenon is an exceedingly general one.[29] Unfortunately, little is known as to the nature of the bonding in the 2:1 compound. It has been suggested that the weak donor opens up one of the two bridges in the dimeric halide to form a singly bridged intermediate. Presumably the bond forces in this singly bridged derivative are related to those responsible for the formation of the doubly bridged dimer.

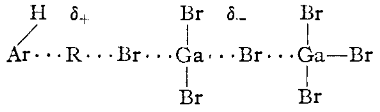
There is also considerable evidence that reactions with Friedel–Crafts catalysts may involve the metal halide either to the first or second power in specific reactions. For example, the exchange of radiobromine between ethyl bromide and aluminum bromide in carbon disulfide solution varies with the square of the concentration of the metal halide.[30] The alkylation of aromatics by alkyl bromides in 1,2,4-trichlorobenzene solution is first order in aluminum bromide,[31] whereas the corresponding reaction of alkyl bromides with aromatics in excess aromatic as solvent is second order in gallium bromide.[32] The reaction of benzoyl chloride with aromatics is first order in aluminum chloride,[8] whereas the catalysis by antimony trichloride is second order in that species.[19]



In the case of the alkylation of the aromatics, it was suggested that in trichlorobenzene the powerful Lewis acid, aluminum bromide, is capable of transferring the alkyl group from bromine to the aromatic without additional assistance. In benzene or toluene as solvent, the weaker Lewis acid gallium bromide is unable to do so, but requires a second mole of catalyst to facilitate the transfer.



$$\overset{\text{H}\ \ \delta_+}{\text{Ar}}\cdots\text{R}\cdots\text{Br}\cdots\overset{\text{Br}\ \ \delta_-}{\underset{\text{Br}}{\text{Al}}}\text{—Br}$$



$$\overset{\text{H}\ \ \delta_+}{\text{Ar}}\cdots\text{R}\cdots\text{Br}\cdots\overset{\text{Br}\ \ \delta_-}{\underset{\text{Br}}{\text{Ga}}}\cdots\text{Br}\cdots\overset{\text{Br}}{\underset{\text{Br}}{\text{Ga}}}\text{—Br}$$

On this basis the second-order term observed in the antimony trichloride catalyzed reaction[19] arises from the requirement of a second mole of the weak Lewis acid to transfer the benzoyl group from the chlorine atom to the aromatic.

The tendency to form dimeric metal halide molecules is well recognized with ferric chloride, gallium chloride and aluminum chloride. A similar tendency probably exists in antimony pentachloride, since the stable 1:2 derivative $(C_6H_5)_2CO{\cdot}2SbCl_5$

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[27] H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953).

[28] S. C. J. Olivier, *Rec. trav. chim.*, **37**, 205 (1918).

[29] H. C. Brown, P. Stehle and P. A. Tierney, THIS JOURNAL, **79**, 2020 (1957).

[30] F. L. J. Sixma and H. Hendriks, *Rec. trav. chim.*, **75**, 29 (1956).

[31] H. Jungk, C. R. Smoot and H. C. Brown, THIS JOURNAL, **78**, 2185 (1956).

[32] C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6345 (1956).

has been reported.[18] On the other hand, boron chloride forms 1:2 compounds only at low temperatures[29] and no instances of stannic chloride exhibiting such behavior are known. Consequently, one could rationalize a fast reaction involving a square term for the chlorides, $SbCl_5$, $FeCl_3$, $GaCl_3$ and $AlCl_3$, with a slow reaction involving a first-order term for $SnCl_4$ and BCl_3.

In this explanation, aluminum chloride, presumably the strongest Lewis acid in the group, is out of place. The reaction of benzoyl chloride–aluminum chloride with aromatics exhibits clean second-order kinetics, first order in the aluminum chloride, and the rate is far slower than that observed for the metal halides exhibiting a square term.

A possible explanation is suggested by a consideration of how the square term may arise in the kinetics. The available evidence is that the strong Lewis acids ($SbCl_5$, $FeCl_3$, $GaCl_3$, $AlCl_3$) exist in benzoyl chloride as 1:1 addition compounds whose stability presumably corresponds with the strength of the metal halide as a Lewis acid. This 1:1 addition compound will be in equilibrium with minor amounts of the 1:2 compound

$$2C_6H_5COCl{\cdot}MX_n \rightleftarrows C_6H_5COCl{\cdot}M_2X_{2n} + C_6H_5COCl$$

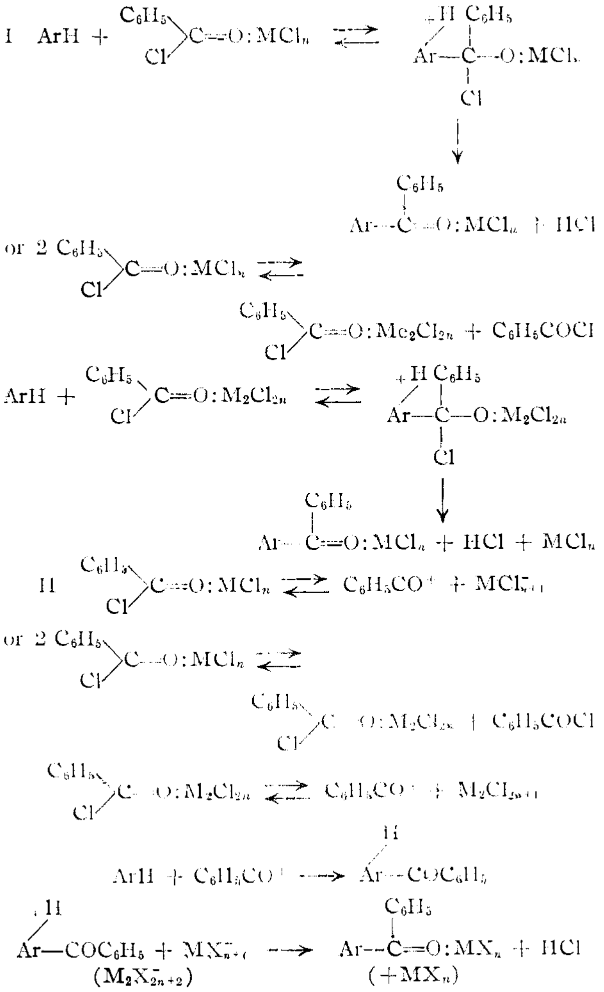
Conceivably the stability of the 1:1 addition compound, $C_6H_5COCl{\cdot}AlCl_3$, is such that the 1:2 compound is incapable of existing in kinetically significant amount in the case of the very strong Lewis acid, aluminum chloride, but is capable of existence with the somewhat weaker Lewis acids, $SbCl_5$, $FeCl_3$ and $GaCl_3$.

Alternatively, the affinity of aluminum for oxygen in the oxonium salt, $C_6H_5(Cl)C{=}O{:}AlCl_3$, may be so much larger than its affinity for chlorine, that the formation of the dimeric species fails to compete with the excess benzoyl chloride. It may be recalled that in the absence of excess acid chloride, aluminum halides have a pronounced catalytic effect upon the reaction rate. In the case of the other metal halides, $SbCl_5$, $FeCl_3$ and $GaCl_3$, it may be that their affinity for halogen may compete with their affinity for oxygen more effectively than in the case of aluminum chloride. Unfortunately, we do not have data to permit a test of this point.[33]

In summary, we are able to account for the observations in terms of two possible reaction paths, one involving a reaction of a 1:1 complex, $C_5H_5COCl{\cdot}MCl_n$, and the second involving the reaction of a 1:2 complex, $C_6H_5COCl{\cdot}M_2Cl_{2n}$, the latter produced as a reactive intermediate by the reaction of two molecules of the 1:1 complex.

Two basically different mechanisms have been considered for the benzoylation reaction, a direct reaction of the benzoyl chloride–metal chloride addition compound with the aromatic I and a conversion of the benzoyl chloride–metal chloride into acylonium ions II. In II the ions may exist separated or as ion pairs.

Unfortunately, it is not possible to distinguish between these two mechanisms on the basis of the kinetics. Baddeley and Voss[34] demonstrated that halogen exchange occurs between aluminum halides and 2,4,6-tribromo- and 2,4,6-trimethylbenzoyl halides, and concluded that exchange occurs through formation of acylonium ions. They argued for an ionization mechanism for the acylation reaction with these compounds since a direct reaction on the markedly hindered acyl halide–aluminum halide addition compound by the aromatic would produce a highly strained transition state.



The low *ortho* isomer formed in the benzoylation reaction[35] argues for an intermediate of high steric requirements such as is found in the simple addition mechanism. In terms of this mechanism, the vast difference in rates observed for the acylation reaction would be attributed to the major difference in the electrophilic nature of the acid chloride addition compound.

Such differences in the activities of the attacking species should result in major changes in the isomer distribution. Moreover, oxonium addition compounds of the various metal chlorides as well as their dimeric species should vary considerably in their steric requirements. On this basis it is difficult to account for the relatively constant amount of the *ortho* isomer realized in the acylation of toluene, as well as the essentially constant *para/meta* ratio (Table XV).

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(33) We are presently studying the interaction of methyl chloride and dimethyl ether with these metal halides in the hope of obtaining quantitative data on this question; work in progress with J. Byrne and G. L. Klender.

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

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

The relative reactivity of benzene to chlorobenzene in the aluminum chloride-catalyzed reaction is 87,[8] whereas a comparison of the data in Tables III and IV in the much faster gallium chloride reaction indicates an essentially identical value, 80. Here also the results are in better accord with an attack by the benzoylonium species.

In terms of the proposed kinetic expression 3, the reaction involving the 1:2 complex is accompanied by an inhibition term first order in the total concentration of the metal halide catalyst. This inhibition can be accounted for simply in terms of the ionic mechanism. Production of $[M_2X_{2n+1}]^-$ anions in large quantities by other processes besides II would depress the acylonium ion concentration by the common ion effect and result in inhibition. These processes would essentially be reactions involving the acid couple, HX, M_2X_{2n}. However, until more data are available on the precise state of the metal halides in benzoyl chloride solution[14] it appears fruitless to discuss these questions further.

The major differences in the kinetics for the various catalysts can be accounted for in the stage leading to the production of the carbonium ion. In this interpretation, the subsequent stage, the reaction of the acylonium ion with the aromatic, proceeds to give products essentially independent of the particular metal halide present.

Experimental Part

Materials.—The benzoyl chloride was purified and handled in the manner described previously.[8] The chlorobenzene was purified by rectification in a column rated at 70 plates and had the physical constants b.p. 131° (745 mm.), $n^{20}\text{D}$ 1.5247. The benzene, toluene and *m*-xylene had known purities of at least 99.5%.

The gallium chloride was prepared by the interaction between hydrogen chloride and gallium metal and purified by resublimation, m.p. 77°, colorless crystals. The stannic chloride was purified by distillation through a specially constructed Vigreux column which contained no joints. The material was first distilled from mercury and a constant boiling fraction retained, b.p. 113.2° (745 mm.). This fraction was reintroduced into the apparatus, the apparatus evacuated and sealed from the atmosphere, and then the material was distilled into ampoules which were later sealed off. The material was obtained as a colorless, clear liquid. The antimony trichloride, m.p. 73°, colorless crystals, and the antimony pentachloride, b.p. 58° (7 mm.), clear yellow liquid, were purified in a similar manner. Ferric chloride was purified by sublimation at low pressure. Prior to the first sublimation, the material in the sublimation tube was heated to about 250° to drive off the small amount of water present. The first sublimation was carried out in a stream of chlorine, and the last two sublimations were carried out at 2 mm. A small amount of material remained behind in each of the last sublimations which apparently was due to slight decomposition. The material was crystalline, green-black to reflected light and vermillion to transmitted light. Boron trichloride (Matheson Chemical Co.) was transferred through a phosphorus pentoxide tube into the reaction solution and used without further purification.

Kinetic Measurements.—The reactions were followed by removing aliquots of the benzoyl chloride solutions, hydrolyzing them with 4 *M* sodium hydroxide, then isolating and weighing the ketones formed in the reactions.[8] The identity of the products was confirmed by infrared examination. All concentrations are in moles liter^{-1}.

Gallium Chloride.—This catalyst dissolves readily in benzoyl chloride to form a colorless solution which exhibits no change over several days. The solution remains colorless upon addition of the aromatic component. The products, as isolated from the reaction solution, were pure isomeric ketone mixtures and contained no detectable impurities or side products.

Because the kinetics of the reaction are unusual (expression 3) and questions might arise concerning the treatment of the data, the results from several experiments are given in Table XVII.

TABLE XVII

KINETIC DATA FOR THE GALLIUM CHLORIDE-CATALYZED BENZOYLATION OF CHLOROBENZENE IN BENZOYL CHLORIDE SOLUTION AT 25°

$[GaCl_3]$ 0.1014 *M* $[C_6H_5Cl]$ 0.305 *M*		$[GaCl_3]$ 0.202 *M* $[C_6H_5Cl]$ 0.304 *M*		$[GaCl_3]$ 0.510 *M* $[C_6H_5Cl]$ 0.305 *M*	
Time, min.	[Ketone], *M*	Time, min.	[Ketone], *M*	Time, min.	[Ketone *M*
28.2	0.0131	25.2	0.0202	24.2	0.0419
83.2	.0267	80.5	.0535	79.4	.1131
145.5	.0405	142.2	.0706	140.5	.1547
197.2	.0480	194.1	.0845	192.8	.1790
250.2	.0530	248	.0958		

Ferric Chloride.—Ferric chloride readily dissolves in benzoyl chloride to form an apparently stable, highly colored, solution.

The third-order plots of the data fell off in varying degrees during the latter stages of the reactions with chlorobenzene and the results were not highly reproducible. Part of the irregularity probably was due to the difficulty of obtaining pure ferric chloride. A further complication occurred in the step where the ketone was extracted from the sodium hydroxide solution in which the sample from the reaction was hydrolyzed. The basic ferric salts were present as finely divided suspension and clear separations of the extraction solvent phase did not occur. Although some of the other catalysts gave precipitates in the hydrolysis step, the interference due to these precipitates was not serious except in the case of ferric chloride.

Antimony Pentachloride.—Due to the low solubility of antimony pentachloride in benzoyl chloride the initial concentration of antimony pentachloride was not varied. The data were reproduced easily and satisfactory third-order plots were obtained.

Stannic Chloride.—Stannic chloride mixes with benzoyl chloride to form a colorless solution which remains colorless upon standing. When toluene is added, the solution turns light yellow-green or light orange immediately and then slowly turns green. After about 1000 minutes, the solution has become very dark green. A similar color is observed if the reaction solution containing aluminum chloride as catalyst is allowed to stand for several days. When aluminum chloride is used as the catalyst, the reaction is essentially complete in 60 minutes, after which time the reaction mixture is colorless. The reaction utilizing stannic chloride is only a fraction as rapid although the color starts developing immediately. Although the major products formed in the reaction with toluene are the isomeric methylbenzophenones, the infrared spectra indicate the presence of side products.

When samples of the reaction mixture were shaken with 4 *M* sodium hydroxide in order to stop the reaction, the green color disappeared only slowly. It has been reported previously that certain molecular addition compounds containing stannic chloride possess striking stability toward water.[25]

Boron Trichloride.—The reaction mixtures were essentially colorless. Only the initial phase of the reaction with toluene was investigated. Precise data could not be obtained because of the apparent volatility of the boron trichloride above the reaction mixture. The infrared spectrum was ill-defined, indicating the presence of impurities in the product.

Antimony Trichloride.—The reaction mixtures, initially colorless, gradually turned light green after several days. With initial concentrations $[SbCl_3]$ 0.917 *M* and $[C_6H_5CH_3]$ 0.387 *M*, after 11,600 minutes had elapsed, 12 mg. of an unidentified material was obtained.

LAFAYETTE, INDIANA