solution was formed.[24] After acidification with cold dilute hydrochloric acid, the aqueous layer was separated and extracted four times with ether. The combined ether solution was washed with saturated sodium chloride and dried over magnesium sulfate. The ethereal solution was concentrated to a volume of 200 ml. and hydrogenated at room temperature and 40 lb. pressure with 0.8 g. of platinum oxide catalyst. Within a few minutes 96% of the theoretical amount of hydrogen was absorbed.

After removal of the catalyst by filtration, the ether solution was extracted with 100 ml. of cold 10% sodium hydroxide in four portions. The aqueous layer was acidified to congo red with cold hydrochloric acid and extracted four times with chloroform. The chloroform was distilled and by distillation of the residue a 1.2 g. (15%) yield of 3-methylcyclohexanecarboxylic acid, b.p. 79–80° (0.04 mm.), $n^{25}\text{D}$ 1.4583, neut. equiv. 142.3 (calcd. 142.2), was obtained. The infrared spectrum of this product corresponded in detail to a composite of the spectra of the isomeric 3-methylcyclohexanecarboxylic acids.

The ether solution from which the acid was extracted was washed once with saturated sodium chloride and dried over potassium carbonate. The ether was distilled and distillation of the residue gave 3.6 g. (55%) of 3,3′-dimethylbicyclohexane, b.p. 140–145° (29 mm.), $n^{25}\text{D}$ 1.4746, d^{25}_4 0.872, $M\text{D}$ 62.7 (calcd. 62.6).

Anal. Calcd. for $C_{14}H_{26}$: C, 86.51; H, 13.49. Found: C, 86.33; H, 13.47.

The infrared spectrum of this material had bands at 3.15 μ (carbon–hydrogen bond), 6.90 μ (carbon–carbon bond) and 7.25 μ (terminal methyl group). This product arises from coupling during the Grignard reaction and is presumably a mixture of all or some of the six possible diastereoisomers.

F. (***cis*-5-Methyl-2-cyclohexenyl Chloride**).—When 8.0 g. (0.061 mole) of *cis*-5-methyl-2-cyclohexenyl chloride and 22.4 g. (0.92 atom) of magnesium was treated under the same conditions as Part E, 103% of the theoretical amount of hydrogen was absorbed, and a 3.2 g. (37%) yield of 3-methylcyclohexanecarboxylic acid, b.p. 81–82° (0.09 mm.), $n^{25}\text{D}$ 1.4583, neut. equiv. 142.3 (calcd. 142.2) was obtained. The infrared spectrum of this product was indistinguishable from that of the product derived from the *trans*-chloride and corresponded in detail to that of a binary mixture of IIa and IIb.

Lithium Aluminum Hydride Reduction of 3,3-Dimethylcyclohexanecarboxylic Acid. A. 3,3-Dimethylcyclohexanecarboxylic Acid from Grignard Reaction.—An ethereal solution of 1.75 g. (0.011 mole) of the 3,3-dimethylcyclohexanecarboxylic acid, $[\alpha]^{25}\text{D}$ −0.011° (*l* 1 dm., neat), obtained by carbonation of the Grignard reagent derived from (−)-3,3-dimethylcyclohexyl chloride, $[\alpha]^{24}\text{D}$ −2.37° (*l* 1 dm., neat) was added to a solution of 1.5 g. (0.04 mole) of lithium aluminum hydride in 30 ml. of anhydrous ether. The resulting mixture was hydrolyzed with 5% hydrochloric acid, and the aqueous phase was extracted with ether. After removal of the ether 1.2 g. (77%) of inactive 3,3-dimethylcyclohexylcarbinol, b.p. 89° (10 mm.), $n^{25}\text{D}$ 1.4598, 3-nitrophthalate m.p. 203.4–204.4° (lit.[10] b.p. 89–92° (8 mm.), 3-nitrophthalate m.p. 200.5–202.5°), was obtained. The melting point of authentic 3-nitrophthalate, m.p. 203.8–204.6° (prepared by the method of Doering and Beringer[10]), was not depressed when mixed with the 3-nitrophthalate from the above reduction.

B. Optically Active 3,3-Dimethylcyclohexanecarboxylic Acid.—*dl*-3,3-Dimethylcyclohexanecarboxylic acid was resolved by dissolving 31.2 g. (0.2 mole) of inactive acid and 65 g. (0.2 mole) of quinine in dry acetone, and recrystallizing the resultant salt twice from dry acetone. The salt was hydrolyzed with dilute hydrochloric acid to give (−)-3,3-dimethylcyclohexanecarboxylic acid, b.p. 99.5–100° (0.12 mm.), $[\alpha]^{26}\text{D}$ 1.14° (*l* 1 dm., neat). Reduction of 1 g. (0.0064 mole) of this active acid by the same procedure as in Part A gave 0.6 g. (66%) of (−)-3,3-dimethylcyclohexylcarbinol, b.p. 89° (10 mm.), $n^{25}\text{D}$ 1.4600, $[\alpha]^{24}\text{D}$ 2.07° (*l* 1 dm., neat).

Infrared Analysis.—Determinations of the isomeric composition of the mixtures of *cis*- and *trans*-3-methylcyclohexanecarboxylic acid from the Grignard reactions were carried out using a Baird Associates recording infrared spectrophotometer, model B. The spectra were taken of 5% solutions of the samples in carbon disulfide in 0.1 mm. sodium chloride cells. The percentage compositions were determined by comparison of the spectra of the samples with those of synthetic mixtures of the pure isomeric 3-methylcyclohexanecarboxylic acids using the absorbancies at 7.86 and 8.04 μ.

The amount of isomeric impurity in the 3-methylcyclohexyl chlorides was estimated by using absorbancies at 7.48 and 14.68 μ and assuming additive absorbancies at these wave lengths.[30] The samples were run as pure liquid films in 0.041-mm. sodium chloride cells.

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[30] E. I. Stearns in M. G. Mellon, "Analytical Absorption Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 369.

Madison 6, Wisconsin

[Contribution from the Richard B. Wetherill Laboratory of Purdue University]

Kinetics of the Friedel–Crafts Benzoylation of Benzene with Aluminum Chloride as Catalyst and Benzoyl Chloride as Solvent[1,2]

By Herbert C. Brown and Frederick R. Jensen[3]

Received September 26, 1957

In benzoyl chloride as solvent, aluminum chloride brings about the quantitative benzoylation of benzene. The reaction exhibits simple second-order kinetics, first order in aluminum chloride and first order in benzene, with the second-order rate constant being essentially independent of the initial concentration of the reactants. On the assumption that the aluminum chloride exists in benzoyl chloride solution as the addition compound, $C_6H_5COCl{\cdot}AlCl_3$, the reaction proceeds in accordance with the equation 1 and the rate expression is given in equation 3. From the variation in the rate constant with temperature, $\Delta H^{\ddagger} = +15.1$ kcal./mole and $\Delta S^{\ddagger} = -27.2$ e.u. Substitution of a portion of the benzoyl chloride solvent by cyclohexane results in a decrease in the rate constant. Thus the observed relative rates are 1, 1/4, 1/13, 1/22 in solvents containing 0, 25, 51 and 74% cyclohexane, respectively. Possible reaction mechanisms consistent with the observed kinetics are considered.

The Friedel–Crafts acylation reaction appeared to possess certain desirable features for our studies of the factors influencing the catalytic effectiveness of polyvalent metal halides and the effect of substituents on the rate of aromatic substitution. For these objectives we required a reaction with relatively simple kinetics.

The kinetics of the Friedel–Crafts acylation re-

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[1] The Catalytic Halides. XXI. Directive Effects in Aromatic Substitution. XXI.

[2] Based upon a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree.

[3] Research assistant on a project supported by the Atomic Energy Commission, 1953–1954; National Science Foundation Predoctoral Fellow, 1954–1955.

action have been examined in a number of solvents.[4-9] However, there apparently exists no clear-cut example of simple kinetics in any solvent.[10] The observed rate constants increase with increasing initial concentration of the acyl halide–aluminum halide complex in toluene,[4,5] carbon disulfide[6] and benzene[6,7] as solvents. In nitrobenzene as solvent, in which the aluminum chloride must be predominantly complexed with nitrobenzene rather than with benzoyl chloride, the observed rate constants decrease sharply as the initial concentrations of aluminum chloride are increased.[8] Moreover, ternary complexes ($C_6H_5NO_2$, $AlCl_3$, ArH) exist in this system, as evidenced by the formation of highly colored solutions with the more basic aromatic hydrocarbons, such as the polymethylbenzenes.[8] As a result, it was concluded that the system based on nitrobenzene as solvent was not suitable for these studies.

In attempting to select a suitable solvent, benzoyl chloride itself appeared promising. Not only is it a polar medium, but also, as one of the reactants, its use might simplify the kinetics. Accordingly a kinetic investigation was undertaken with this solvent.

Results

In the earlier kinetic studies in non-polar solvents, the reaction rates were determined by following the rate of disappearance of the acid chloride. This procedure obviously was impractical for rate studies utilizing the acyl chloride in large excess, as solvent. After considering a number of alternatives, we settled on the isolation of the reaction product, benzophenone, from aliquots of the reaction mixture, and its measurement by direct weighing.

In order to realize consistent results, it was necessary to exert special care in the purification of the reagents, especially benzoyl chloride, and to design special apparatus to permit forming, storing and transferring the solutions under anhydrous conditions. Fortunately, the standard solutions of aluminum chloride were both colorless and stable over periods of several weeks, and no significant changes in rate constants were observed using either freshly prepared or relatively old standard solutions of aluminum chloride in benzoyl chloride. Moreover, with the addition of benzene the reaction proceeded smoothly, and the reaction mixtures remained both colorless and homogeneous throughout the reaction period.

In the presence of excess benzene, one mole of ketone is formed quantitatively for each mole of aluminum chloride. On the assumption that the aluminum chloride exists in benzoyl chloride in the form of the simple addition compound, $C_6H_5COCl \cdot AlCl_3$, the reaction may be expressed by equation 1.

$$C_6H_5COCl \cdot AlCl_3 + C_6H_6 \longrightarrow (C_6H_5)_2CO \cdot AlCl_3 + HCl \quad (1)$$

However, it was observed that the reaction does not come to a complete halt. On further standing, the weight of the initial mole of product, per mole of metal chloride, increased at a very slow rate. This subsequent reaction is very slow and no attempt was made to measure the kinetics.

The kinetics of the reaction with benzene were studied in detail at 50°. For individual experiments, second-order kinetics were observed (Table I).

TABLE I

TYPICAL RATE DATA FOR THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF BENZENE IN BENZOYL CHLORIDE SOLUTION AT 49.9°

Time, min.	Benzophenone G.	Benzophenone M	Reaction, %	Rate constant[a] k_2, l. mole^{-1} min.$^{-1}$
8.7	0.0545	0.0598	27	....
22.4	.0869	.0942	43	0.0214
29.9	.1028	.1128	51	.0231
41.6	.1166	.1280	58	.0209
49.3	.1304	.1431	65	.0230
63.4	.1451	.1592	72	.0225
89.3	.1648	.1808	82	.0227
122.7	.1783	.1956	89	.0220
191.9	.1933	.2120	96	(.0234)
2066	.2148	.2357	107[b]	
			Av.	0.0222 ± 0.0007

[a] Initial concentrations: $[AlCl_3] = 0.220$ M; $[C_6H_6] = 0.904$ M. [b] Includes slow subsequent reaction.

The initial concentration of benzene was varied from 0.235 to 0.904 M, and that of aluminum chloride was independently varied from 0.220 to 0.915 M. No significant change in the value of the second-order rate constant was observed (Table II).

TABLE II

SUMMARY OF SECOND-ORDER RATE CONSTANTS FOR THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF BENZENE IN BENZOYL CHLORIDE SOLUTION AT 49.9°

Reagents, M $[AlCl_3]$	$[C_6H_6]$	Rate constant k_2, l. mole^{-1} min.$^{-1}$
0.228	0.470	0.0231
.223	.699	.0226
.220	.904	.0222
.470	.235	.0231
.452	.452	.0226
.915	.475	.0226

From the variation in the rate constants with temperature, the enthalpy and entropy of activation were calculated. The data are summarized in Table III.

The effect of the polarity of the solvent upon the reaction rate was examined by substituting cyclohexane for various amounts of the benzoyl chloride. A decrease in the second-order rate constant was observed with the increasing fraction of cyclohexane present in the mixed solvent (Table IV).

Finally, consideration of possible mechanisms for the reaction made it desirable to examine the effect of hydrogen chloride on the reaction rate. How-

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

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

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

(7) H. Ulich and G. Heyne, *Z. physik. Chem.*, **41**, 509 (1935); H. Ulich and P. V. Fragstein, *Ber.*, **72**, 620 (1939).

(8) H. C. Brown and H. L. Young, *J. Org. Chem.*, **22**, 719, 724 (1957); H. C. Brown, B. Bolto and F. R. Jensen, *ibid.*, **23**, 000 (1958).

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

(10) Recently Smeets and Verhulst (ref. 9) reported simple second-order kinetics for benzene and bromobenzene as solvents. These results appear to be inconsistent with the results of other workers. See footnote 12, F. R. Jensen, THIS JOURNAL, **79**, 1226 (1957).

TABLE III

RATE CONSTANTS AND DERIVED DATA FOR THE ALUMINUM CHLORIDE-CATALYZED BENZOYLATION OF BENZENE IN BENZOYL CHLORIDE SOLUTION

Temp., °C.	25.0	39.9	49.9
Rate constant, k_2	0.00297	0.0100	0.0227
l. mole^{-1} min.$^{-1}$	±0.00011		±0.0007
No. of expts.	3	1	17
Energy of activation, E_{act}		15.8 kcal./mole	
log A		7.28	
Enthalpy of activations, $\Delta H^{\ddagger}$		15.1 kcal./mole	
Entropy of activation, $\Delta S^{\ddagger}$		−27.2 e.u.	

ever, no difference in rate was observed for solutions which were saturated with this gas prior to reaction. Moreover, identical results were obtained with sealed ampules, in which the hydrogen chloride formed in the course of the reaction was confined, and open ampules from which the hydrogen chloride could escape.

TABLE IV

EFFECT OF CYCLOHEXANE–BENZOYL CHLORIDE MIXTURES UPON THE MAGNITUDE OF THE SECOND-ORDER RATE CONSTANT AT 49.9°

Cyclohexane, vol. %	Reactants, M [AlCl$_3$]	[C$_6$H$_6$]	Rate constant k_2, l. mole^{-1} min.$^{-1}$	Rel. rate
0	0.228	0.470	0.0231	1.00
25	.231	.453	.00571	1/4
51	.239	.465	.00182	1/13
74	.245	.485	.00105	1/22

Discussion

The kinetic results clearly indicate that a solution of aluminum chloride in benzoyl chloride reacts with benzene to form benzophenone by a reaction whose rate exhibits clean second-order kinetics (2).

$$\text{rate} = k_2[\text{AlCl}_3][\text{C}_6\text{H}_6] \qquad (2)$$

Since benzoyl chloride is the solvent, the order with respect to this component could not be determined. However, it is well known that benzoyl chloride and aluminum chloride react to form a 1:1 addition compound.[11]

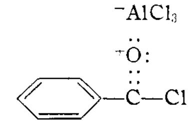
In non-polar solvents Kohler found the molecular weight of the compound $C_6H_5COCl \cdot AlCl_3$ to correspond to that of the dimeric formula,[12] while Ulich has reported that the apparent molecular weights of this and similar addition compounds vary considerably with concentration.[13] Unfortunately, no data are available on the physical state of benzoyl chloride–aluminum chloride in benzoyl chloride solution.

The basic properties of nitrobenzene are very similar to those of benzoyl chloride.[14] Nitrobenzene also forms a 1:1 addition compound, $C_6H_5NO_2 \cdot AlCl_3$, which exhibits higher molecular weights in non-polar solvents,[12,13] but the simple monomeric molecular weight in the polar solvent nitrobenzene.[15] At 20°, the dielectric constant for benzoyl chloride is 23, and the value for nitrobenzene is 36.[16] Consequently, it appears reasonable to assume that the addition compound in benzoyl chloride is present in the simple unassociated, monomeric form, $C_6H_5COCl \cdot AlCl_3$.

On this basis, the rate expression 2 can be modified to include the benzoyl chloride reactant (3).

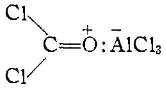
$$\text{rate} = k_2[\text{C}_6\text{H}_5\text{COCl}\cdot\text{AlCl}_3][\text{C}_6\text{H}_6] \qquad (3)$$

Meerwein proposed the ionic structure, $RCO^+ AlCl_4^-$, for the addition compounds of acid chlorides and aluminum chloride.[17] This attractive formulation received wide acceptance in discussions of the mechanism of Friedel–Crafts acylation.[18] The alternate structure $R(Cl)C{=}O{:}AlCl_3$ was suggested by Pfeiffer.[19] However, his proposal has been largely ignored until recently. The available data on ultraviolet spectra,[20] heats of formation[20] and infrared spectra[21] are far better in accord with the un-ionized oxonium structure (4).



(4)

Moreover, Huston and Lang recently examined the rate of chloride exchange of aluminum chloride in phosgene solution.[22] Here also the aluminum chloride must exist as a 1:1 addition compound, $COCl_2 \cdot AlCl_3$. In dilute solution at 25° the exchange is slow with a half-life of approximately 5 hours. Consequently, here also the structure of the addition compound must be that of an oxonium derivative (5).



(5)

It therefore appears that any mechanism proposed to account for the kinetics and other features of the acylation reaction must begin with the oxonium structure for the addition compound.

The simplest mechanism would be one involving a direct reaction of the aromatic with the addition compound.[19,23]

This mechanism will give the observed kinetics if either k_1 or k_2 is rate controlling.

The fact that the addition compound exists predominantly in the form of the oxonium structure does not eliminate the possibility that this structure may exist in equilibrium with a small

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[11] G. Perrier, *Compt. rend.*, **116**, 1298 (1893); W. Nespital, *Z. physik. Chem.*, **B16**, 153 (1932).

[12] E. P. Kohler, *Am. Chem. J.*, **24**, 385 (1900); **27**, 241 (1902).

[13] H. Ulich, *Z. physik. Chem. (Bodenstein-Festband)*, **152**, 423 (1931).

[14] Unpublished observations of Dr. Sang Up Choi, Purdue University.

[15] R. E. Van Dyke and H. E. Crawford, THIS JOURNAL, **73**, 2018 (1951).

[16] A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," National Bureau of Standards Circular 514, 1951.

[17] H. Meerwein, *Ann.*, **455**, 227 (1927).

[18] F. Fairbrother, *J. Chem. Soc.*, 503 (1937); E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 260; R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 333.

[19] P. Pfeiffer, "Organisch Molekulverbindungen," Ferdinand Enke, Stuttgart, 1927, pp. 88, 409.

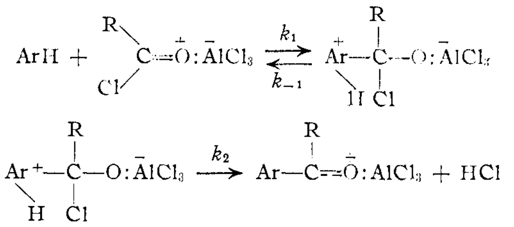
[20] N. N. Lebedev, *J. Gen. Chem. (U.S.S.R.)*, **21**, 1788 (1951).

[21] B. P. Susz and I. Cooke, *Helv. Chim. Acta*, **37**, 1273 (1954); I. Cooke, B. P. Susz and C. Herschmann, *ibid.*, **37**, 1280 (1954).

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

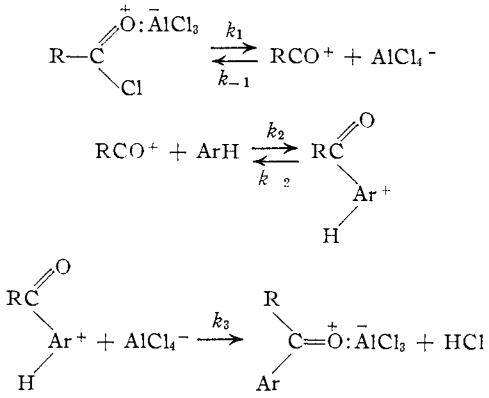
[23] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956.

Mechanism I

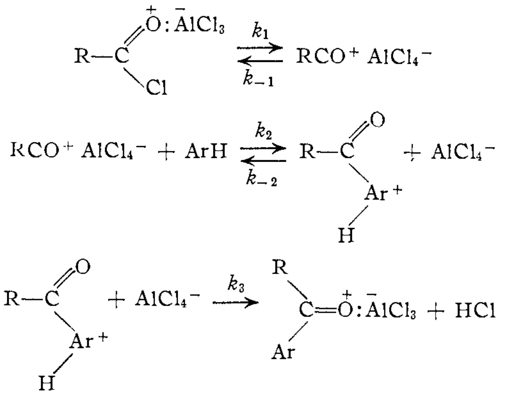


quantity of acylonium ions[24] (mechanism II) or ion-pairs (mechanism III).

Mechanism II



Mechanism III



In mechanism II, if the reaction of the acylonium ion with the aromatic were rate determining, the kinetic expression would be

$$\text{rate} = k(C_6H_5COCl\cdot AlCl_3)^{1/2}(ArH) \qquad (6)$$

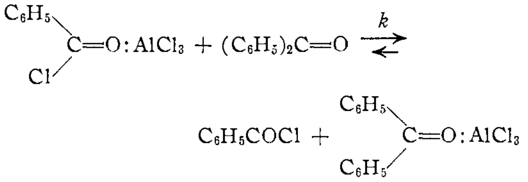
Obviously, this does not correspond to the observed kinetics and this possibility can be eliminated. However, if the third step, the decomposition of the σ-complex is rate-determining, this mechanism would correspond to the observed kinetics.

In mechanism III the conversion of the addition compound to an ion-pair is postulated. This mechanism corresponds to the observed kinetics with either the second stage, the reaction of the aromatic with the ion-pair, or the third stage, the decomposition of the σ-complex, being rate-determining.

The moderate solvent effect is perhaps in better accord with the direct reaction of the aromatic with the addition compound I or with the ion-pair III, than it is with a mechanism involving the formation of separated ions. Baddeley and Voss have argued for a mechanism involving acylonium ions on the basis of their observation that aromatic hydrocarbons react readily with 2,4,6-tribromobenzoyl chloride in the presence of aluminum halide.[24] Certainly, the addition of a hydrocarbon to such a severely hindered carbonyl group as that present in the un-ionized addition compound (mechanism I) appears highly improbable.

The data presently available do not permit a final decision as to the preferred mechanism. We are continuing our studies of this system in the hope of obtaining data which will permit a decision on this point.

In kinetic experiments utilizing excess benzene in benzoyl chloride as solvent the reaction proceeds in accordance with second-order kinetics until one mole of benzophenone is formed for each mole of aluminum chloride, followed by a much slower subsequent reaction. Baddeley and Voss[24] have attributed the ability of the ketone to suppress the reaction to association of the ketone with some reaction intermediate. However, irrespective of the precise mechanism which is followed (I–III), the suppression of the acylation reaction appears to be primarily the result of marked differences in the basic properties of the benzoyl chloride and benzophenone (7).[25]



$$(C_6H_5)(Cl)C{=}O{:}AlCl_3 + (C_6H_5)_2C{=}O \overset{k}{\rightleftarrows} C_6H_5COCl + (C_6H_5)_2C{=}O{:}AlCl_3 \qquad (7)$$

In this way the presence of one mole of benzophenone in the reaction mixture per mole of aluminum chloride will reduce greatly the amount of benzoyl chloride–aluminum chloride addition compound, and the rate of benzoylation will fall off markedly, even in the presence of excess benzoyl chloride and benzene. However, since the equilibrium 7 should decrease, but not eliminate entirely the concentration of benzoyl chloride–aluminum chloride, the rate of the benzoylation reaction would be expected to decrease, but not to halt completely following the formation of one mole of product per mole of aluminum chloride. As the data in Table I reveal, the initial fast reaction, 97% complete in 192 min., continues past 100% at a much slower rate, with 107% of benzophenone formed in 2066 min.

In conclusion, the reaction of benzoyl chloride–aluminum chloride with benzene in benzoyl chloride solution proceeds by a simple second-order reaction, first order in each of the two reactants. The available data are consistent with a mechanism involving a rate-determining reaction of the aromatic with the addition compound, either in its oxonium

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[24] G. Baddeley and D. Voss, *J. Chem. Soc.*, 418 (1954).

[25] Quantitative data on the relative basicity of benzoyl chloride and benzophenone are not available. However, Lebedev (ref. 20) determined the heats of reaction of aluminum bromide with benzoyl bromide and benzophenone to be 14.3 and 19.9 kcal./mole, respectively. It is probable that the difference in the stabilities of benzoyl chloride–aluminum chloride and benzophenone–aluminum chloride is similar.

form I or with a small equilibrium concentration of an ion-pair species III. The kinetics are also consistent with a mechanism involving reaction of the aromatic with free acylonium ions II provided the decomposition of the σ-complex is rate-determining.

Irrespective of the finer details of the mechanism, the simple kinetics should make this reaction a valuable tool in investigating the effect of substituents on the rates of aromatic substitution and the relative catalytic efficiencies of various Friedel–Crafts catalysts.

Experimental Part

Materials.—In the initial stages of this investigation we were uncertain whether stable solutions of aluminum chloride in benzoyl chloride could be prepared. Thus Wertyporoch and Firla[26] reported that with time their solutions of aluminum chloride in benzoyl chloride exhibited an increase in conductance and a darkening in color. Similarly, Ulich[13] reported that the addition compound $C_6H_5COCl\cdot AlCl_3$ is brown in color.

After trying several different procedures for purifying benzoyl chloride, we discovered that repeated fractionation of the material at 4 mm. through a glass-helices packed column rated at 50 plates on occasion yielded material which did not darken upon addition of aluminum chloride. To obtain such material it was important to avoid the presence of porous porcelain or silicon carbide boiling chips, as well as hydrocarbon or silicon greases on the ground joints of the apparatus.

Benzoyl chloride obtained in this way, even though it remained colorless in the presence of dissolved aluminum chloride, exhibited a relatively fast rate in the initial stages of the benzoylation reaction. This difficulty could be avoided by treating the benzoyl chloride with 3 mole % aluminum chloride and 3 mole % toluene. After standing overnight, the unreacted benzoyl chloride was distilled off at 1–2 mm., and the product then was fractionated carefully through the all-glass column, b.p. 56° at 4 mm.

The benzoyl chloride obtained in this way formed standard solutions of aluminum chloride which were perfectly clear and colorless for approximately 10 days. With these solutions the reaction mixtures remained colorless throughout the reaction period, the kinetics of the reaction were reproducible, and the benzoylation went cleanly to 100% completion with either the benzene or the aluminum chloride present in limiting amount.

The aluminum chloride (J. T. Baker Co.) was purified by repeated slow sublimation at 50 mm. Only the highly purified material, crystalline and entirely colorless, was used in the kinetic studies.

The sublimation tubes were constructed from joined sections of 22 mm. and 16 mm. tubing, each of which had a number of constrictions. The larger tubing served as sections for the initial sublimations, while the smaller diameter sections served as ampoules to collect the pure product. A loose plug of glass wool was inserted into the larger tube at the first constriction, followed by a 3-cm. layer of granular aluminum. The aluminum chloride then was inserted, followed by a second plug of glass wool, and the end of the tube sealed off. The tube was then evacuated through the open end to 10 mm., and the aluminum chloride was heated in an electric tube furnace just below the sublimation temperature for several hours to decompose any hydrated aluminum chloride present. When hydrogen chloride was no longer evolved, 50 mm. of dry nitrogen was introduced, and the open end of the tube sealed. The tube was inserted in the furnace to cover the packed section and most of the next section. The temperature was maintained at a level where the aluminum chloride slowly sublimed. When approximately 80% of the aluminum chloride had condensed in the second section, the first section was sealed off and the operation repeated. In this way, after a number of sublimations, the aluminum chloride was finally distributed in the several sections of the smaller tubing, sealed and ready for utilization.

Benzene was purified by fractionation followed by fractional crystallization. The product used exhibited a purity of at least 99.8% by cooling curve analysis.

Preparation of Solutions.—Standard solutions of aluminum chloride in benzoyl chloride were prepared and stored in the apparatus shown in Fig. 1. The apparatus was carefully dried. The ampoule of aluminum chloride, prepared as described above, was scratched with a file, and the scratch touched with a hot rod in such a manner that the glass cracked, but did not break open to the atmosphere. The weighed ampoule was then placed in side-arm A and the end sealed off. The apparatus was evacuated and then shaken until the cracked ampoule opened. The aluminum chloride was then sublimed into the apparatus and the constriction in the side-arm sealed off. The glass fragments of the ampoule were weighed to determine the weight of the aluminum chloride.

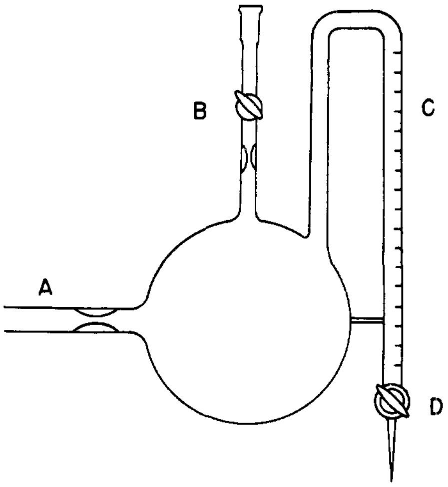

Fig. 1.—Storage flask for standard solutions of aluminum chloride in benzoyl chloride.

The apparatus was now weighed, then benzoyl chloride was fractionated in through B, and the apparatus weighed again to determine the weight of the benzoyl chloride. The constriction in B was sealed off. A glass enclosed magnetic bar facilitated solution of the aluminum chloride.

The side-arm C was constructed from a Pyrex buret for dispensing purposes. Purified nitrogen (~250 mm. above atmospheric pressure) was introduced into the apparatus through side-arm C to facilitate removal of the solution. The buret was filled by tipping the entire apparatus. From the weights of the aluminum chloride and benzoyl chloride, their concentrations were calculated using the density of the solution, determined by utilizing the buret side-arm. The 3-way stopcock made it possible to clean the tip of the buret.

Although the procedure was relatively difficult, the standard solutions obtained in this manner proved to be quite stable and yielded kinetic data of high reproducibility.

Analytical Procedure.—Attempts to follow the reaction by titrating the hydrogen chloride evolved, or by measuring its volume at constant pressure, failed to give reproducible results. The procedure utilizing the isolation of benzophenone and its measurement by weighing proved to be satisfactory.

An aliquot of the reaction mixture was added to excess 4 *M* sodium hydroxide with rapid shaking in order to stop the reaction. The solution was boiled for 40 min. to hydrolyze the benzoyl chloride. After cooling, the solution was extracted with three successive 5-ml. portions of distilled chloroform. Each portion was washed with 50 ml. of distilled water and each wash solution returned to the alkaline solution before the next extraction. The chloroform extracts were collected in weighed 30-ml. bottles containing a few small silicon carbide boiling chips.

The bottles were placed in a vacuum desiccator containing a concentrated solution of benzophenone in alcohol. The pressure was reduced slowly by means of an aspirator to permit smooth evaporation of the chloroform without bumping. Finally, the pressure was permitted to drop to 10–15 mm. The bottles were taken out and weighed every

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[26] E. Wertyporoch and T. Firla, *Z. physik. Chem.*, **162**, 398 (1932).

10 hr., until the rate of loss in weight became constant (approximately 0.5 mg. per 10 hr. period). Appropriate small corrections were applied to the data to correct for this loss of weight.

This procedure was thoroughly tested with blank experiments. Known samples of benzophenone of 0.1 to 0.3 g. in benzoyl chloride could be determined with an error of approximately 2 parts per 1000. The procedure also was tested by comparing the gravimetric results with an ultraviolet analysis utilizing the peak at 2540 Å. Close agreement was realized.

TABLE V

COMPARISON OF ANALYSES FOR BENZOPHENONE IN A KINETIC RUN BY GRAVIMETRIC AND SPECTROSCOPIC (ULTRAVIOLET) PROCEDURES

Time, min.	Benzophenone, g. Gravimetric[a]	Benzophenone, g. U.v. analysis	Deviation
35	0.0488	0.0487	−0.0001
100	.1087	.1092	+ .0005
215	.1677	.1678	+ .0001
310	.1998	.1984	− .0014
405[b]	.2219	.2235	+ .0016

[a] Adjusted, as described in text. [b] 55% reaction.

Kinetic Procedure.—The reactions were carried out in calibrated reaction vessels fitted with ground glass stoppers, with a side-arm just below the mouth. This side-arm was connected to a nitrogen supply with a pressure approximately 3 cm. above atmospheric, so that removal of the stopper immediately resulted in a flow of dry nitrogen out of the mouth of the flask.

The desired amount of the standard solution of aluminum chloride was transferred from the buret (Fig. 1) to the calibrated reaction vessel and diluted with pure benzoyl chloride to the desired concentration. The solution was brought to the desired temperature in a constant temperature bath (±0.01°) and the reaction initiated by adding the benzene from a special all-glass hypodermic syringe, followed by vigorous stirring. This item was constructed by drawing the end of a glass syringe into a long capillary. The amount of benzene was determined by weighing the syringe before and after adding the aromatic to the reaction mixture. In some cases relatively concentrated solutions were used and it was feared that the usual assumption of additive volumes of the various solutions might lead to significant errors. Therefore, the volume of the reaction solution was noted and the concentrations were calculated using this volume.

At appropriate intervals of time aliquots were removed with pipets and analyzed for benzophenone as described above. The tips were cut from these pipets to increase the rate of flow. The amount delivered by the pipet varied markedly with the temperature of the reaction solution and the rate of flow from the pipet. Consequently, the pipets were calibrated with benzoyl chloride at the appropriate temperature, with the pipet at room temperature. Fortunately, this procedure permitted the delivery of reproducible, constant aliquots of the reaction mixtures.

Data for a typical kinetic study are reported in Table I.

LAFAYETTE, INDIANA

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

Relative Rates of the Aluminum Chloride-catalyzed Benzoylation of Representative Benzene Derivatives in Benzoyl Chloride Solution. Partial Rate Factors for the Benzoylation of Toluene[1,2]

BY HERBERT C. BROWN AND FREDERICK R. JENSEN[3]

RECEIVED SEPTEMBER 26, 1957

Second-rate constants for the benzoylation reaction (aluminum chloride in benzoyl chloride) were determined for a number of representative benzene derivatives. The relative reactivities at 25° are: benzene, 1.00; toluene, 110; *t*-butylbenzene, 73; chlorobenzene, 0.0115; *o*-xylene, 1120; *p*-xylene, 140; *m*-xylene, 3940. The isomer distribution in the benzoylation of toluene under these conditions is 9.3% *ortho*, 1.45% *meta* and 89.3% *para*. From the relative rates and isomer distributions the partial rate factors for the benzoylation of toluene under these conditions are calculated to be: o_f, 30.7; m_f, 4.8; p_f, 589. These partial rate factors are in excellent agreement with the Selectivity Relationship. The rates calculated from these factors for the benzoylation of the three xylenes are in fair agreement with the observed rates. Finally, the rates of benzoylation of the monosubstituted benzenes correlate well with the σ^+ constants.

The acylation of aromatics is a simple substitution reaction with desirable characteristics for our studies both of directive effects in aromatic substitution and of the role of Lewis acid catalysts on the rates of Friedel–Crafts reactions. Our first attempts to study the benzoylation of aromatics for this purpose utilized nitrobenzene as a solvent.[4] Unfortunately, in this solvent the reaction exhibited complex kinetics with respect to the aluminum chloride. Moreover, in the case of the higher methylbenzenes deeply colored solutions were obtained which pointed to the formation of ternary complexes involving nitrobenzene, aluminum chloride and the aromatic.[5]

The observation that the benzoylation of benzene with aluminum chloride in benzoyl chloride solution exhibits simple second-order kinetics[6] encouraged us to examine the utility of this reaction for our purposes. Accordingly a study was undertaken of the rates of benzoylation of toluene, *t*-butylbenzene, chlorobenzene, *o*-, *m*- and *p*-xylene, and of the isomer distribution in the benzoylation of toluene. A related study of the effect of various Friedel–Crafts catalysts on the reaction rate will be reported in a later publication.

Results

The benzoylation of toluene was carried out in the identical manner previously utilized for benzene.[6] The reaction proceeded smoothly to the formation of methylbenzophenones in essentially quantitative yield. Since the rates were much greater than in the corresponding reaction of benzene, a lower range of temperatures was utilized to obtain the enthalpy and entropy of activation.

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(1) Directive Effects in Aromatic Substitution. XXII.

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

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

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

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

(6) H. C. Brown and F. R. Jensen, THIS JOURNAL, **80**, 2219 (1958).