

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF TULANE UNIVERSITY]

**Kinetics of the Friedel-Crafts Reaction, and Activity of Mixed Catalysts in the Reaction of Benzoyl Chloride with Toluene**

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It has been observed frequently that relatively impure, technical aluminum chloride is a more active catalyst for certain Friedel-Crafts reactions than the c. p. reagent. The activity of a catalyst is here considered as the velocity of a given reaction produced by it as distinguished from the yield of product obtained. The latter point has been investigated by Riddell and Noller,<sup>1</sup> who determined the yields of a number of ketones and hydrocarbons obtained with various mixtures of ferric and aluminum chlorides, and by Boswell and McLaughlin,<sup>2</sup> who determined the total amounts of hydrogen chloride evolved by the reaction of chloroform and benzene using similar mixtures. Studies of the velocity of reaction of benzoyl and benzyl chlorides with toluene, using pure aluminum chloride and pure ferric chloride, have been made by Steele,<sup>3</sup> and of similar reactions with benzene by Olivier.<sup>4</sup> Both concluded that these reactions involve complexes of catalyst and reagent, and that the reactions are unimolecular when less than one mole of catalyst is used, if the toluene is in large excess. The reactions proceeded smoothly to completion, and Riddell and Noller,<sup>1</sup> using mixed catalysts, also obtained good yields in the synthesis of benzophenone.

Steele's method in which the hydrogen chloride was removed by a constant stream of hydrogen and titrated was more rapid and convenient than Olivier's, in which the unreacted benzoyl chloride had to be hydrolyzed and the benzoic acid extracted with ether for titration. Olivier adopted the latter procedure after criticizing the uncertainty of Steele's analytical method, the uncertainty of the simpler method being due obviously to the possibility that the hydrogen chloride is not removed completely by the hydrogen. We found that the removal of the acid from solution is in fact much slower than was supposed by Steele, who plotted a curve for the desaturation of a saturated solution of hydrogen chloride in toluene and corrected his titrations by adding the amounts

(1) W. A. Riddell and C. R. Noller, *THIS JOURNAL*, **52**, 4365 (1930); **54**, 290 (1932).

(2) M. C. Boswell and R. R. McLaughlin, *Can. J. Res.*, **1**, 400 (1929).

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

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

remaining dissolved at corresponding times as read from this curve. Actually the removal of the hydrogen chloride is approximately a unimolecular process, the rate of removal being proportional to the concentration in solution. If the initial reaction is unimolecular there are two consecutive unimolecular processes, and the amount,  $x$ , removed and titrated in time  $t$  is given by the equation

$$x = a - ak_2e^{-k_1t}/(k_2 - k_1) + ak_1e^{-k_2t}/(k_2 - k_1) \quad (1)$$

in which  $k_1$  is the velocity constant of the initial reaction,  $a$  is the initial concentration of the reacting complex in the Friedel-Crafts reaction, and  $k_2$  is the velocity constant for the desaturation of the solution.<sup>5</sup> Solving for the required velocity constant gives

$$k_1 = -(1/t) \ln \{ (k_1/k_2)(e^{-k_2t} + (x - a)/a) - (x - a)/a \} \quad (2)$$

for which values of  $k_1$  must be found by approximation. The value of the constant obtained from the simple unimolecular law for the later stages of the reaction is a useful first approximation, as it differs only slightly from  $k_1$  when  $t$  is large; two successive applications of Newton's method usually yield a value of  $k_1$  which is within the limits of accuracy of the experimental data.

The desaturation of the solution by hydrogen is only approximately unimolecular under suitable conditions and  $k_2$  depends upon the volume of solution used. If  $c$  is the variable concentration of hydrogen chloride in solution, its partial pressure in the gas in equilibrium is  $p_{\text{HCl}} = Kc$ , from Henry's law. The respective volumes of gases and vapor in unit volume of saturated gas are

$$V_{\text{HCl}} = p_{\text{HCl}}/760$$

$$V_{\text{T}} = p_{\text{T}}/760$$

$$V_{\text{H}_2} = (760 - p_{\text{T}} - p_{\text{HCl}})/760$$

The volume of toluene vapor,  $V_{\text{T}}$ , is practically constant as the toluene is in large excess and its concentration does not change appreciably. Unit volume of dry hydrogen leaves the solution as saturated gas of volume  $760/(760 - p_{\text{T}} - p_{\text{HCl}})$ , in which the volume of hydrogen chloride is  $p_{\text{HCl}}/(760 - p_{\text{T}} - p_{\text{HCl}})$ . Substituting for the partial pressure of hydrogen chloride in terms of

(5) K. Jablczyński, *Z. anorg. Chem.*, **60**, 38, (1908); see also J. B. Cohen, "Organic Chemistry," 1924, Vol. I, 365.

its concentration gives  $Kc/(760 - p_T - Kc)$ , and since  $p_T$  is practically constant it is possible to put  $b = (760 - p_T)/K$ , obtaining for the rate of removal of hydrogen chloride

$$dx/dt = kc/(b - c)$$

If the constant term  $b$  is large compared to  $c$ , as is the case in the experiments under consideration, the denominator may be combined with the velocity constant  $k$  to give

$$dx/dt = k_2c$$

In these equations  $x$  is the amount of hydrogen chloride removed and titrated, while  $c$  is its concentration in solution, and in order to integrate either it is necessary to express  $c$  and the initial concentration of reacting complex, in terms of  $x$  and the initial amount,  $a$ , of reacting complex, and the volume of solution,  $v$ . This leads in the simpler case to a unimolecular equation

$$k_2/v = (1/t) \ln a/(a - x)$$

except that the volume of solution must be taken into account in the manner indicated if it is not the same in all experiments, as was the case in Steele's investigation.

The experiments to be described in this report were concerned with three objectives: first, to determine the relative activities of several samples of aluminum chloride in two distinct types of the Friedel-Crafts reaction; second, to determine the activity as measured by the reaction velocity of benzoyl chloride with toluene of a series of mixtures of aluminum and ferric chloride covering a wide range of composition; and third, to investigate the significance of the data obtained by Steele's method when the constants are calculated by equation (2). Since commercial aluminum chloride containing iron was most active in the benzoyl chloride reaction, it seemed likely that ferric chloride might be responsible for the higher activity. This is further indicated by the variations in the yield curves of the reactions studied by Riddell and Noller<sup>1</sup> when ferric chloride was added, showing that it affects the course of the reactions in a specific manner. It has also been claimed that aluminum chloride is activated for use in the Gattermann-Koch synthesis by small additions of titanium chloride or mixtures of titanium and ferric chlorides.<sup>6</sup>

### Experimental

**Apparatus and Procedure.**—The apparatus was the same as that used by Steele<sup>3</sup> except for the supply of hy-

drogen which was drawn from a commercial cylinder through a suitable system of reducing valves, dried by sulfuric acid, and measured by a calibrated flowmeter. In order to obtain a constant reading the gas passed through the meter under a static pressure of 50 to 75 mm., for which the necessary correction was made in each experiment. Variations in the rate from one experiment to another were corrected on the basis that the desaturation velocity constant varies in direct proportion to the hydrogen rate, other conditions being constant.

We found it preferable to weigh the catalysts used in thin glass bulbs which were broken by a plunger at the instant the watch was started, which minimized the absorption of moisture and permitted more accurate determination of the zero time. The benzoyl or benzyl chloride was dissolved in the toluene, the first increment of 2.5 or 5.0 cc. of standard sodium hydroxide was run into the absorber, and phenolphthalein added. The hydrogen was next turned on and adjusted and finally the catalyst bulb was broken. Benzoyl or benzoyl chloride was not carried over into the absorber in amounts sufficient to give an appreciable titer either while adjusting the hydrogen rate or after the reaction was complete.

**Materials.**—The toluene was c. p., sulfur-free grade, dried by standing over sodium.

The benzoyl and benzyl chlorides were c. p. grade, and were freshly distilled in quantities sufficient for each series of experiments, a constant boiling middle third fraction being collected in each case in glass-stoppered bottles which were kept in a desiccator. Samples were weighed rapidly into a weighing bottle.

Aluminum chloride samples of several grades were used: (1) Mallinckrodt c. p. grade specified to contain 0.1% Fe; (2) Mallinckrodt c. p. containing 0.005% Fe; (3) a purer sample prepared by action of dry hydrogen chloride on the purest aluminum powder available and resublimed, which contained less Fe than the sample marked 0.005%; and (4) Gulf technical grade specified to contain 92.6% AlCl<sub>3</sub>, 3.6% FeCl<sub>3</sub>, 1.04% TiCl<sub>4</sub> and 0.28% SiCl<sub>4</sub>.<sup>7</sup>

Ferric chloride was prepared by the action of chlorine on c. p. iron powder and resublimed.

Mixed catalysts were prepared by weighing the required quantities of Mallinckrodt aluminum chloride containing 0.005% Fe and ferric chloride into small narrow necked tubes. A rod passed through a rubber tube fitted to the neck was used to grind and mix the chlorides until they were sufficiently homogeneous. Samples were transferred directly from the tubes into bulbs exactly as in weighing

TABLE I  
MIXED CATALYSTS

No.	Sample, g.	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> , g.	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (1 cc. = 0.00889 g. Fe) cc.	FeCl <sub>3</sub> , %	AlCl <sub>3</sub> , %	FeCl <sub>3</sub> mole % (aver.)
1	0.5744	...	2.3	10.5	..	..
	.4286	0.1776	1.8	10.8	94.3	9.1
2	.6383	...	13.4	54.3	..	..
	.3668	.1649	7.6	53.2	49.1	48.8
3	.2756	.1276	7.9	74.2	25.6	..
	.5161	.2349	14.7	73.5	24.4	69.9
4	.3745	.1548	2.8	19.3	83.2	16.4

(7) A quantity of this grade was supplied by the Gulf Refining Co.

(6) I. G. Farbenind. A. G., British Patent 334,009 (1929); C. A., 35, 710 (1931).

material for the experiments, and analyzed for aluminum and iron. The mixtures used are given in Table I.

The excess over 100% in the total percentages is a measure of the extent of hydrolysis which unavoidably occurred in weighing and mixing the preparations. The mole percentages were calculated on the basis of the ferric chloride, which was determined directly by electrometric titration. More elaborate precautions to obtain greater accuracy of composition did not seem to be justified at present by the accuracy with which the velocity constants can be determined.

**Determination of Desaturation Velocity.**—Results of two experiments to determine the constant  $k_2$  are given in Table II.

NaOH (0.193 N) (Both experi- ments), cc.	Toluene = 50 cc., 30° H <sub>2</sub> (corr.) = 282 cc./min.		Toluene = 45 cc., 30° H <sub>2</sub> (corr.) = 250 cc./min.	
	Time, min.	$k_2$	Time, min.	$k_2$
20.0	0.70	0.575	0.53	0.641
30.0	1.17	.586	.90	.630
40.0	1.93	.563	1.42	.609
45.0	2.55	.535	1.80	.580
50.0	3.33	.527	..	..
55.0	4.55	.530	2.67	.590
60.0	8.58	.560	3.42	.585
60.5	∞	..	..	..
65.0	..	..	4.78	.573
69.0	..	..	9.50	.522
70.0	..	..	∞	..
Average		0.554		0.587

Using 20.0 cc. of toluene saturated with hydrogen chloride at 25°, Steele<sup>3</sup> obtained the value 1.46 for a hydrogen velocity of 250 cc./min. On calculating this value and the two values given above to the uniform basis of 50.0 cc. of toluene and 250 cc./min. of hydrogen, the values of  $k_2$  are: Steele, 0.584; 1st experiment, 0.491; and 2d experiment, 0.528. These results are in fair agreement, and we used the average of our values,  $k_2 = 0.510$ , in computing our velocity constants, while the higher value given by Steele was used in recalculating his results.

**Determination of Reaction Velocities.**—Table III gives the data of experiment 16 on benzoyl chloride with Gulf technical aluminum chloride as catalyst, which are typical of the results obtained by Steele's method. The values of  $k$  obtained by means of the simple unimolecular equation are to be compared with those of  $k_1$  calculated from equation (2). In this particular experiment the initial reaction is fairly rapid,  $k_1$  being almost as large as  $k_2$ , and both the trend in the  $k$  values and the difference in the magnitude of the two constants are emphasized. In experiments in which  $k_1$  is much smaller than  $k_2$  the discrepancy is less, but is always significant. The values of  $k_1$  are sufficiently constant to permit of averaging with reasonable accuracy for the purposes of the present investigation.

The results of all experiments are summarized in Table IV. The first group of eight experiments shows the velocity of reaction of benzyl and of benzoyl chloride with each of the three commercial grades of aluminum chloride and the resublimed sample. The next nine experiments

TABLE III

NaOH (0.170 N), cc.	Time, min.	$k$ Unimol.	$k_1$ Eq. (2)
3.0	1.12	0.082	0.365
5.0	1.57	.097	.340
7.5	1.93	.128	.388
10.0	2.33	.148	.394
15.0	3.17	.181	.413
20.0	4.23	.205	.409
25.0	5.97	.217	.360
30.0	9.70	.211	.285
34.5	∞	= 0.00587 moles HCl	
Average (excluding last point)			0.381
Mole ratio HCl/AlCl <sub>3</sub>			= 1.16

are those made with the mixed catalysts of Table I, while the last three were made to determine the effect of concentration in increasing the reaction velocity.<sup>4</sup>

**Recalculation of Steele's Results.**—Velocity constants for several representative experiments were recalculated using equation (2) with the results shown in Table V. As Steele gave corrected titrations, the "corrections" were deducted to obtain the original values, but in experiment 17 this was impossible as the "correction" was larger than most of the recorded titers. The average  $k$  values reported by Steele do not differ greatly from  $k_1$  in experiments 1 and 5, in which  $k_2$  is large. In the experiments with benzyl chloride 30 cc. of toluene was used, making  $k_2$  smaller, and the discrepancy is greater. In addition most of Steele's benzyl chloride experiments do not yield constants for  $k_1$ , but show a steady drift between the extreme values given below. We cannot account for this in view of the very satisfactory constants obtained in our experiments with this reagent, even in cases when  $k_2$  was smaller than  $k_1$ .

## Discussion

**Comparison of the Reactions of Benzoyl Chloride and Benzyl Chloride.**—The first eight experiments in Table IV show that the behavior of the three technical samples and the resublimed aluminum chloride is quite different with each of these reagents. With benzoyl chloride the reaction velocity increases as the percentage of ferric chloride present is increased. On the other hand, experiments with benzyl chloride and the same four catalysts show that, while the velocity constant is greatly increased by very small percentages of ferric chloride, it decreases again when substantial amounts are present as in the Gulf technical sample. Steele's observation is confirmed that approximately one mole of catalyst is required per mole of ketone formed, while fifteen to twenty moles of hydrocarbon are produced per mole of catalyst.

TABLE IV  
 SUMMARY OF EXPERIMENTAL RESULTS

Toluene = 50 cc.;<sup>a</sup> Expts. 13-16, 24-26, temp. 30°; Expts. 17-19, temp. 25°

Expt.	Reagent C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl, g.	Catalyst, g.	FeCl <sub>3</sub> mole, %	AlCl <sub>3</sub> moles × 10 <sup>6</sup>	FeCl <sub>3</sub> moles × 10 <sup>6</sup>	HCl/MeCl <sub>3</sub> moles	k <sub>1</sub> (Eq. 2) aver.
13	0.7911	0.0298	0.002	22.3	...	18.3	0.293
14	.5142	.0203	.012	15.2	...	19.0	0.974
9	.7743	.0268	.239	20.1	...	14.4	1.388
6	.7659	.0282	2.98	20.3	0.6	19.4	0.771
C <sub>6</sub> H <sub>5</sub> COCl							
12	1.5173	0.7365	0.002	552	...	1.385	0.050
15	1.4636	.5965	.012	447	...	1.388	.106
2	1.5343	.6570	.239	493	...	1.155	.145
16	1.4926	.6741	2.98	486	1.5	1.205	.381
17	1.5386	.6090	0.012	456	...	1.015	.115
18	1.5922	.6356	9.1	424	43	0.723	.280
28	1.5085	.6366	16.4	385	76	.830	.143
27	1.5742	.6957	48.8	241	231	.610	.203
20	1.5773	.9259	9.1	620	61	.769	.304
23	1.4897	.7874	16.4	476	94	.821	.275
21	2.0220	.9154	48.8	318	304	.640	.625
22	1.5734	.7095	69.9	139	323	0.502	.527
19	1.5115	.5935	100.0	...	365	1.020	.077
24	0.7182	.3312	0.012	248	...	1.000	.088
25 <sup>a</sup>	1.7791	.8600	.012	645	...	1.072	.189
26 <sup>a</sup>	3.4662	1.6993	.012	1271	...	1.003	.354

<sup>a</sup> Toluene, 25 cc.
 TABLE V  
 RECALCULATION OF STEELE'S DATA

Expt.	Reagent	Catalyst	k <sub>2</sub>	k (Unimol.)	k <sub>1</sub> (Eq. 2)
1	C <sub>6</sub> H <sub>5</sub> COCl	AlCl <sub>3</sub>	1.46	0.129	0.138
5	C <sub>6</sub> H <sub>5</sub> COCl	AlCl <sub>3</sub>	1.46	.080	.084
18	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	AlCl <sub>3</sub>	0.974	.533	.757
17	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	AlCl <sub>3</sub>	.974	.258	.580-.315
21	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	FeCl <sub>3</sub>	.974	.104-.260	.140-.301
22	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	FeCl <sub>3</sub>	.974	.037-.112	.044-.114

**Activity of Mixed Catalysts.**—In the ketone synthesis studied all of the mixed catalysts are much more active than either of the samples from which the mixtures were prepared. A significant result of the experiments in this group is the decrease in the ratio of moles of hydrogen chloride produced to the total moles of metal chlorides used, as the percentage of ferric chloride is increased. Pure ferric chloride produces almost exactly one mole of hydrogen chloride per mole of catalyst, as does the aluminum chloride. This indicates that, with mixed catalysts, the ketone formed removes both aluminum and ferric chlorides in the form of a stable complex, and that the reacting substance also probably consists of a complex such as C<sub>6</sub>H<sub>5</sub>COCl·AlCl<sub>3</sub>·FeCl<sub>3</sub>, at least in part. In the case of the catalyst containing 16.4 mole per cent. ferric chloride (experiments 28 and 23) the ratio HCl/AlCl<sub>3</sub> is very nearly unity, which

agrees with a mechanism in which all of the ferric chloride is combined as C<sub>6</sub>H<sub>5</sub>COCl·C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>·AlCl<sub>3</sub>·FeCl<sub>3</sub>, while the remaining aluminum chloride is removed as C<sub>6</sub>H<sub>5</sub>COCl·C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>·AlCl<sub>3</sub>. The other mixtures do not give results agreeing with such a simple mechanism, but all of them definitely indicate the formation of larger complexes involving both chlorides in the molecule.

This explanation is not contradictory to the observation of Riddell and Noller<sup>1</sup> that good yields of benzophenone are obtained with similar mixed catalysts, as their experiments were made with excess of catalyst and at higher temperatures at which the complexes postulated may be unstable. Further evidence in favor of the removal of ferric chloride as part of the final complex is found in Steele's results with benzyl chloride in conjunction with our own. Steele showed that ferric chloride acts practically as a true catalyst in the hydrocarbon synthesis, forming 2500 moles of product per mole of catalyst. If even the small percentage of ferric chloride in the Gulf chloride used for experiment 6 were free to catalyze the reaction independently, it would be sufficient to convert all of the benzyl chloride present. Actually the ratio of product to catalyst is about the same as that obtained with the purest sample of aluminum chloride, and the reaction

stops when considerable excess benzyl chloride still is unconverted.

As Olivier has shown,<sup>4</sup> and we have confirmed, the reaction velocity increases markedly with increase of the concentration of the reacting substance. If the reacting molecules are composed in part of the larger complex involving both chlorides, the effective concentration is less than the total concentration of metal chlorides present. The average velocity constants for the mixed catalysts are plotted against mole per cent. ferric chloride in Fig. 1; curve I is that obtained for experiments in which the total concentration of the metal chlorides was constant, while curve II represents experiments in which the effective concentration of reacting complex was approximately the same, as measured by the hydrogen chloride evolved. The latter curve indicates the large increase in activity of mixed catalysts at comparable concentrations as ferric chloride is

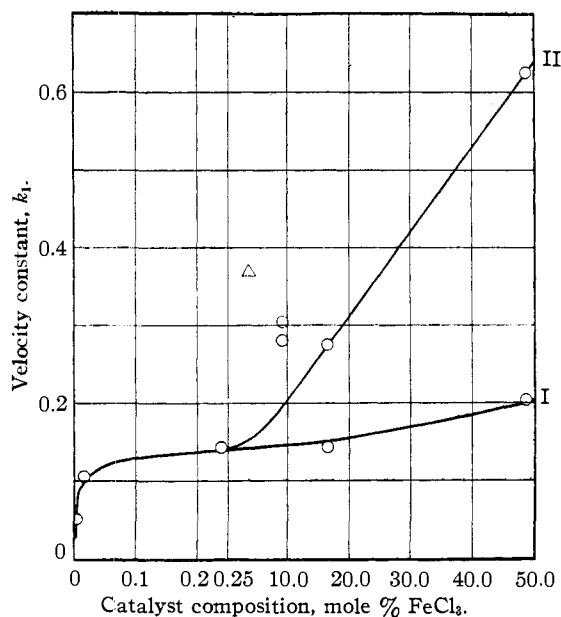


Fig. 1.—(Table IV) Variation of reaction velocity with catalyst composition:  $\Delta$ , Gulf tech.  $\text{AlCl}_3$ ; I, concn. of metal chloride constant; II, concn. of active complex constant.

added. The scale is enlarged for the first 0.25% to include constants for the purer technical samples. The Gulf aluminum chloride is much more active than can be accounted for by its ferric chloride content alone, and its greater activity is probably due in part to the titanium tetrachloride which it contains, the latter being claimed as an activator of aluminum chloride catalysts.<sup>6</sup>

**Effect of Concentration and Order of Reaction.**—The last three experiments in Table IV together with experiments 15 and 17, all of which were made with the same grade of catalyst, show the effect of concentration in increasing the reaction velocity. In Fig. 2 the average velocity constants are plotted against the mole fraction of

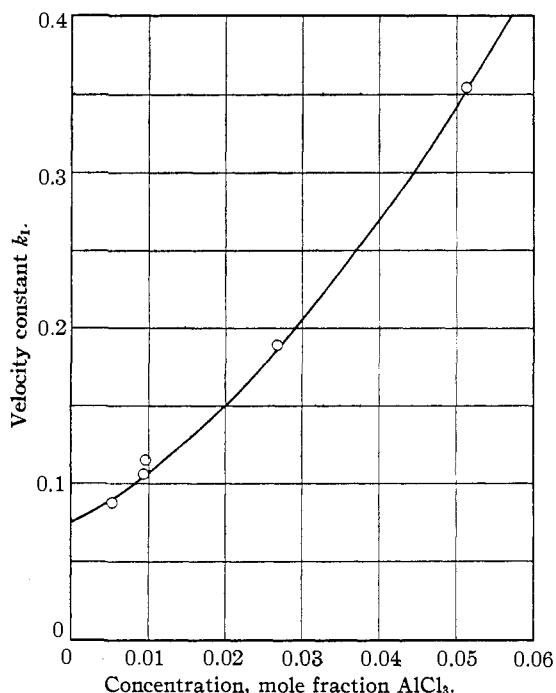


Fig. 2.—(Table IV) Variation of reaction velocity with concentration for  $\text{AlCl}_3$  containing 0.005% Fe.

catalyst used. The increase in  $k_1$  is almost the same in magnitude as that found by Olivier<sup>4</sup> in his work on benzoyl chloride and benzene, and can be represented over the ten-fold range of concentration by  $k_1 = 0.075 + 2.395c + 60.5c^2$ , in which  $c$  is the mole fraction of the reacting substance. The complete reaction is, of course, bimolecular and the constants are understood to represent the pseudounimolecular mechanism obtained by using a large excess of toluene. For this reason the constant would be expected to vary with concentration, but the variation given by  $k_{\text{bimol.}} = k_1/b$ , in which  $b$  is the approximately constant concentration of toluene for each experiment, would be much smaller and in the opposite direction,  $k_1$  decreasing with an increased concentration of catalyst.<sup>8</sup> If it is possible, as postulated above, for the aluminum chloride complex to form a larger complex with ferric chloride which has a higher

(8) F. O. Rice in Taylor, "Treatise on Physical Chemistry," 1925, Vol. II, 874.

activity, Olivier's explanation<sup>4</sup> of association of the aluminum chloride complex itself would seem tenable in accounting for the higher reaction velocity at higher concentrations. Except for this variation, in regard to which independent evidence would be desirable, our method of calculation leads to results in good agreement with a unimolecular reaction order, and may be taken as supporting the mechanism of this Friedel-Crafts reaction previously advanced by Steele.

### Summary

1. A correct method of calculating velocity constants from data obtained by Steele's method has been applied to experiments on the Friedel-Crafts reactions of benzoyl and benzyl chlorides with toluene.

2. The relative order of activity of various catalysts depends upon the type of reaction, and in the case of benzoyl chloride the activity increases with increasing percentage of ferric chloride.

3. Mixed catalysts covering a wide range of composition of aluminum and ferric chlorides have been investigated in respect to the reaction of benzoyl chloride with toluene. At comparable

concentrations the activity increases with increasing mole percentage of ferric chloride and reaches a maximum at percentages in excess of 50 mole per cent.

4. The mixed catalysts have been shown to produce less than one mole of product for each mole of total metal chlorides present. Evidence is given in support of the explanation that this is due to the removal of the catalyst in the form of a bimetal complex with the reaction product, such as  $C_6H_5COC_6H_4CH_3 \cdot AlCl_3 \cdot FeCl_3$ .

5. Variation of the reaction velocity over a ten-fold range of concentration, the toluene being always in large excess, has been determined, and is of the same order of magnitude as that reported in a similar reaction by Olivier. The present work furnishes evidence in support of the explanation of this effect as being due to association of the reacting complex.

6. The new experimental data and method of calculation lead to results in satisfactory agreement with a unimolecular order for the reaction, and thus lend support to the mechanism proposed by Steele.

NEW ORLEANS, LOUISIANA

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## The Chemistry of Mold Tissue. X. The Phospholipides of *Aspergillus Sydowi*<sup>1</sup>

BY D. W. WOOLLEY, F. M. STRONG, W. H. PETERSON AND E. A. PRILL

While several papers have been published dealing with the simple lipides of molds, no report has been found regarding the characterization of the compound lipides. A few workers have reported preliminary analyses of the phospholipides,<sup>2</sup> but no detailed study of these compounds has been reported. In a previous paper<sup>3</sup> the simple lipides of *A. sydowi* have been described; the examination of the phospholipides of this same organism is herein described.

### Experimental Part

**Extraction and Purification.**—The mold was grown for ten days on glucose-inorganic salt medium in large ster-

ilized incubators.<sup>4</sup> While still growing it was removed from the medium, washed with cold water, squeezed out by hand and dried rapidly at 30–60° in air. Two batches of mycelium were grown at intervals of eight months and the phospholipides of each batch examined separately. The phospholipides from the first batch will be designated as A, and those from the second batch as B. A was extracted from 7.27 kg., and B from 3 kg. of dry mold.

The mold was extracted continuously for about a week in a Lloyd type extractor. A was obtained by extraction with alcohol, and B by extraction with alcohol-ether (1:1). The solution from the extractor was evaporated, and the residue redissolved by adding water and ether. (In this and subsequent operations air was excluded by a stream of carbon dioxide.) The two layers were separated, filtered and the water layer discarded. A very small amount of matter remained undissolved in both preparations. The water layer contained only traces of nitrogen and phosphorus, and contained mannitol.

The ether layer was concentrated, and poured into a

(1) This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

(2) (a) Aso, *J. Tokyo Chem. Soc.*, **20**, 921 (1900); (b) Takata, *J. Soc. Chem. Ind., Japan*, **32**, 171B (1929); (c) Thomas, *Am. J. Botany*, **17**, 779 (1930).

(3) Strong and Peterson, *THIS JOURNAL*, **56**, 952 (1934).

(4) Peterson, Pruess, Goricca and Green, *Ind. Eng. Chem.*, **25**, 213 (1933).