

*Citation:*

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example of BIGELOW, for the elimination of the 11 year period the departures from the nearest 60 months (5 years) have been calculated and not those from the normal of the whole period

Comparison teaches that in the beginning till 1891 the barometercurve shows indeed much conformity with the prominence curve; afterwards however every similarity has vanished and in the later years in which the prominences hardly show any variation, the barometeroscillation goes on with the same regularity as before. Therefore very likely the connection during the first years has been only accidental.

Wettevreden, 10 October 1912.

**Chemistry.** — “*Dynamic researches concerning the reaction of FRIEDEL and CRAFTS.*” By S. C. J. OLIVIER and Prof. J. BÖSEKEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of December 28, 1912).

Dynamic researches have already been carried out with  $\text{AlCl}_3$  or analogous substances as catalyst.

The first are those of A. SLATOR<sup>1)</sup>, who investigated the action of chlorine on benzene in the presence of  $\text{SnCl}_4$  and  $\text{FeCl}_3$ .

The absorption of the halogen dissolved in an excess of benzene was measured, and it was found that this proceeded according to the reaction scheme of the first order the constant being proportional to the amount of the catalyst.

We may conclude therefrom that the catalyst is constantly active; that its action is not sensibly altered by any of the reaction products.

Further we mention the research of B. D. STEELE<sup>2)</sup>, who has studied the ketone synthesis and the formation of phenyltolylmethane under the influence of  $\text{AlCl}_3$  and  $\text{FeCl}_3$ , where the progressive change of the reaction was determined from the amount of hydrogen chloride evolved.

<sup>1)</sup> Proc. 19, 135 (1903); Journ. Chem. Soc. 83, 729 (1903); Zeits. phys. Ch. 45, 513 (1903).

L. BRUNER had carried out measurements as to the bromination of benzene, but as a catalyst iodine was used which is not directly comparable with  $\text{AlCl}_3$ ; moreover it was not sufficiently taken into consideration that the bromine unites with the catalyst (see Dissertation S. C. J. OLIVIER).

SLATOR has also used iodine as catalyst. Although this research is very interesting as regards the benzene substitution, this part may be passed over for the reason stated.

<sup>2)</sup> Journ. Chem. Soc. 83, 1470 (1903).

Although, in our opinion, this *modus operandi* (see Dissertation C. S. J. OLIVIER) cannot be expected to give accurate results it was rendered probable by him that, when in the ketone synthesis the proportion  $\text{AlCl}_3 : \text{C}_6\text{H}_5\text{COCl}$  is smaller than (or at most only equal to) unity, the reaction was of the first order. With an excess of  $\text{AlCl}_3$ , a reaction of the second order would have to be assumed where the  $\text{AlCl}_3$  would combine with the acid chloride as well as with the toluene.

The latter course of reaction would always have to be assumed with  $\text{FeCl}_3$  as catalyst. The figures found by him for the synthesis of phenyltolylmethane differ so much that they do not admit of a safe conclusion.

Much more regular are the figures obtained by H. GOLDSCHMIDT and H. LARSEN<sup>1)</sup> in their research on the chlorination of nitrobenzene and the benzylation of anisole in the presence of substances such as  $\text{SnCl}_4$  and  $\text{AlCl}_3$ .

They obtained the result that the reaction was of the first order and that the constant was directly proportional with the concentration of the catalyst.

As in the chlorination of benzene, the action of the catalyst appears not to be disturbed by the reaction products.

If we consider that  $\text{AlCl}_3$  unites with the nitrobenzene as well as with the anisole to molecular compounds, and that these substances were always present in large excess, this result is not a matter of great surprise.

The catalyst is then greatly paralysed, which condition cannot be modified to any extent by the formation of chloronitrobenzene (benzylanisole, respectively) in small quantities in regard to the nitrobenzene (anisole, respectively).

That in the benzylation of anisole  $\text{AlCl}_3$  is not very active is shown by the fact that this reaction could still be measured at  $25^\circ$  in a  $N/10$  solution of  $\text{AlCl}_3$ , although as a rule the hydrogen atoms of anisole are much more readily substituted than those of benzene.

The exceedingly slow chlorination of nitrobenzene at  $50^\circ$  may be due to the paralytic condition of the catalyst as well as to the lesser activity of the benzene hydrogen atoms.

From this survey as to what has been carried out in this direction it follows that a systematic research under various conditions was very much to be desired.

The only somewhat trustworthy results were obtained in the

<sup>1)</sup> Zeitschr. phys. Ch. 48, 424 (1904).

chlorination of benzene with  $\text{SnCl}_4$  (SLATOR) and in the just mentioned research of GOLDSCHMIDT and LARSEN in which, however, neither the progressive change of the reaction nor the rôle of the catalyst has been much elucidated.

For this reason we have more closely studied the reaction between p-bromophenylsulphonchloride and benzene.

It was first our intention to carry this out in a neutral solvent for which carbon disulphide was chosen; it appeared, however, that the reaction then took quite another course<sup>1)</sup> so that we were compelled to choose the hydrocarbon itself as the solvent.

The p-bromosulphonchloride was prepared from bromobenzene by sulphonating this with fuming sulphuric acid, neutralising the mixture with lime and converting the calcium salt by means of sodium carbonate into the sodium salt; the sodium p-bromosulphonate thus obtained was converted by  $\text{PCl}_5$  into the chloride. This was freed from  $\text{POCl}_3$  with cold water and recrystallised from ether.

We had chosen the sulphonchloride as starting point because this is not decomposed by cold water, whereas it is rapidly decomposed on warming with aqueous silver nitrate, so that the unattacked sulphonchloride could be freed, by means of cold water, from the  $\text{AlCl}_3$  and the  $\text{HCl}$  formed and afterwards be titrated with silver nitrate solution of known strength.

The benzene hydrocarbons were dried carefully over  $\text{AlCl}_3$  and kept in stock with exclusion of moisture.

The measurements were carried out by making (with exclusion of light and moisture) a solution of definite quantities of sulphonchloride, aluminium chloride, and hydrocarbon; from time to time a definite volume of this solution was withdrawn and analysed.

For details we refer to the dissertation of Mr. OLIVIER which will appear shortly.

We reprint therefrom a few series of analyses.

The benzene required for this was treated before the reaction with  $\text{AlCl}_3$  and distilled; a thiophene-free benzene which had not thus been dried and distilled exhibited a small initial value and a strong course of the constant.

From table I we see that the reaction between 1 mol. of  $\text{AlCl}_3$  and 1 mol. of acid chloride is one of the first order; when, however, 80 % of the original quantity has been converted a serious retarda-

<sup>1)</sup> It then proceeded according to the scheme:  $\text{Br C}_6\text{H}_4\text{SO}_2\text{Cl} + \text{AlCl}_3 + \text{C}_6\text{H}_6 = \text{Br C}_6\text{H}_4\text{SO}_2\text{AlCl}_2 + \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ .

TABLE I.

Action of  $\text{BrC}_6\text{H}_4\text{SO}_2\text{Cl}$  (1 mol.) +  $\text{AlCl}_3$  (1 mol.) on excess of benzene.  
 Concentration acid chloride = 0.1 n.;  $T = 30^\circ$ .  
 $(a-x)$  = concentration acid chloride in grammols. after the time  $t$  in minutes  
 $K_I$  = constant monomolecular reaction.  
 $K_{II}$  = " bi " " "

$t$	$(a-x)10^3$	$K_I$	$K_{II}$
0	86.1	—	—
120	75.3	0.00111	0.0139
240	66.4	0.00108	0.0144
360	59.2	0.00104	0.0146
480	50.6	0.00111	0.0170
720	39.2	0.00109	0.0193
1500	21.5	[0.00093]	—
4320	19.3	[0.00035]	—

TABLE II.

Action and concentration as above. Benzene not again dried.

$t$	$(a-x)10^3$	$K_I$
0	82.1	—
60	78.7	0.000698
210	71.8	0.000636
1320	50.6	0.000367

tion is noticed. We attribute this: 1<sup>st</sup> to the absorption of moisture during the manipulations, which exerts an influence particularly when the amount of the active catalyst has become small;

2<sup>nd</sup> to a slight paralysis caused by the reaction itself.

*Influence of the temperature.*

TABLE III.

As in table I, temperature = 40°

	$(a-x)10^3$	$K_1$
0	—	—
30	61.6	—
90	52.3	0.00273
165	43.1	0.00251

The proportion  $\frac{K_t + 10}{K_t} = \pm 2,5$ , is therefore normal.

*Influence of the concentration.*

TABLE IV.

As in table I. Concentration of  $AlCl_3$  as well as of  $BrC_6H_4SO_2Cl = 0.2$  n  
(The expression  $\frac{1}{2}(a-x)10^3$  indicates the percentages of the acid chloride originally present.)

	$\frac{1}{2}(a-x)10^3$	$K_1$
0	36.6	—
120	28.1	0.00220
300	19.6	0.00208
540	14.7	0.00169

The much more rapid progress of the reaction compared with that of the  $N/10$  concentration was shown by the fact that after scarcely a quarter of an hour, which is the time required to obtain a homogeneous solution, more than 65 % of the original quantity had already been converted.

The constant for the  $N/5$  concentration is twice that of the  $N/10$  concentration.

We should conclude from this, that the entire course of the reaction can be represented by the reaction:

$$\frac{dx}{dt} = kC_{AlCl_3}(a-x)$$

that is to say, of a monomolecular reaction influenced catalytically,

in which the velocity of the reaction is proportional to the amount of chloride present and to the quantity of the catalyst.

In that case, at a given concentration of the catalyst, a change of the initial concentration of the acid chloride should not cause any modification in the value of the constant.

If, however, we take an excess of acid chloride we obtain the following :

TABLE V.

Concentration  $\text{AlCl}_3 = 0.1 \text{ n.}$ ; acid chloride =  $0.15 \text{ n.}$ ;  $t = 30^\circ$ .

$t$	$\frac{2}{3} \times (a-x)10^3$	$K_I$	$K'_I$
0	90.8	—	—
120	83.9	0.000656	0.00106
240	77.5	0.000662	0.00110
360	72.5	0.000617	0.00105

TABLE VI.

Concentration  $\text{AlCl}_3 = 0.1 \text{ n.}$ ; acid chloride =  $0.2 \text{ n.}$ ;  $t = 30^\circ$ .

$t$	$\frac{1}{2} \times (a-x)10^3$	$K_I$	$K'_I$
0	89.7	—	—
185	82.0	0.00487	0.00117
370	76.6	0.00427	0.00108
585	70.9	0.00402	0.00110

Herein  $K_I$  has been calculated as if all the acid chloride present is concerned in the reaction, hence in accordance with the above schema, whereas  $K'_I$  has been calculated as if only the acid chloride which has formed a molecular compound with the  $\text{AlCl}_3$ , enters into reaction.

It is easy to see that, only on the latter supposition, we obtain a constant without course and which agrees with the constant obtained with equimolecular quantities of acidchloride- $\text{AlCl}_3$  (concentration  $N/10$ ).

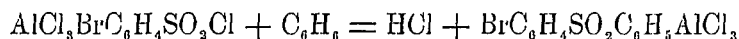
The excess of acidchloride is therefore quite inactive; only that acidchloride which is combined with the aluminiumchloride is active.

Hence in connection with the preceding; applies the relation :

$$\frac{dx}{dt} = K \times C_{AlCl_3} \times C_{BrC_6H_4SO_2Cl \cdot AlCl_3}$$

In solution of one of the active molecules, the velocity of reaction is therefore proportional to the quantity of the other molecule, in so far as this has united with the catalyst, as well as with the total quantity of the catalyst.

The part thereof which during the reaction passes to the sulphon:



although not capable of rendering the acid chloride active must retain its catalytic activity in other respects.

We may explain this by assuming that  $AlCl_3$  renders active the benzene, with which it forms *no* compound, *never mind whether the catalyst is united to the sulphonchloride or to the sulphon*<sup>1)</sup>.

If the above relation is correct, the addition of an equivalent amount of sulphon to the catalyst before or during the reaction must either prevent or stop the same, because one of the necessary molecules cannot, or no longer, be rendered active.

From Table VIIa and b this appears really to be the case.

TABLE VIIa and b.

a $AlCl_3 = 0.1$ n.; sulphonchloride = 0.1 n. sulphon = 0.1 n.		b As in a; the sulphon 0.1 n has been added after all had become homogeneous.	
t	(a-x)10 <sup>3</sup>	t	(a-x)10 <sup>3</sup>
0	99.2	0	83.6
180	99.3	155	83.9
500	99.8	435	83.6
		1200	85.5

If on the other hand our explanation is correct, an excess of  $AlCl_3$ , which cannot then be paralysed either by the sulphonchloride or by the sulphon, must exert a perceptibly stronger action. For we have assumed that the catalyst renders active the benzene also and it will do this undoubtedly better still when it is in looser combination; this is also confirmed by the experiment. (Table VIII).

<sup>1)</sup> It is possible and even probable that the action of the  $AlCl_3$  does undergo a *slight* change; the course of the constant (see table I) might be partly attributed to this.



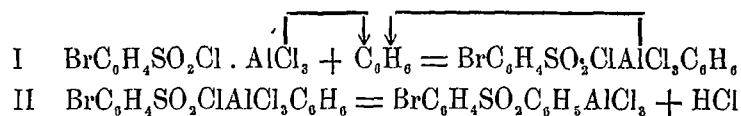
TABLE VIII.  
 $\text{AlCl}_3 = 0.2 \text{ n}$ ; sulphonchloride = 0.1 n.

$t$	$(a-x) 10^3$	$K_1$	
0	60.8	—	The $\text{AlCl}_3$ remained undissolved to a considerable extent.
45	38.0	0.0104	
105	17.3	0.0120	
240	3.4	0.0120	

When compared with table I, the reaction constant has become 10 times greater; also it is constant till the end. The lesser value at the commencement will, probably, have been caused by the fact that the benzene was not yet saturated with the catalyst which is but slightly soluble therein.

Hence, it must be observed that the relation given above only applies to partly paralysed  $\text{AlCl}_3$ ; the free aluminiumchloride has a much more powerful action.

We can now go a step further. The above reaction may be imagined to take place in two phases:



The first (I) represents the real catalytic reaction which shows us the formation of a ternary compound, called by one of us the dislocation.

[This dislocation applies here to the benzene because that of the other molecule in the formation of  $\text{BrC}_6\text{H}_4\text{SO}_2\text{Cl} \cdot \text{AlCl}_3$  has already taken place before the starting of the reaction. The arrows indicate that the benzene is rendered active by *all* the  $\text{AlCl}_3$ ].

The second (II) is the elimination of the hydrogen chloride.

If now we supposed that I would proceed with infinite velocity in regard to II we should measure the reaction of decomposition of the ternary compound and the constant thereof could not be dependent on the concentration of the aluminium chloride. Only by assuming that I proceeds slowly in regard to II we obtain the course of the reaction as found by us<sup>1)</sup>.

<sup>1)</sup> Not the existence of a similar ternary compound is, therefore, essential because the course of the reaction shows that it breaks up, but the act of its formation called by one of us dislocation. (Also compare Dissertation H. J. PRINS Delft 1912 p. 12 and 54).

The research which is being continued in different directions in order to confirm the result obtained has elucidated the catalytic action of  $\text{AlCl}_3$ , thus far that it does *not* exert its action because it unites with one of the molecules, for the free  $\text{AlCl}_3$  was much more active than the combined portion. The view already expressed many times by one of us that the catalytic action of aluminium chloride is based on an influence (called by him *dislocation*) which makes itself felt before the real compound is formed, has, therefore, been confirmed by this research.

In harmony therewith it appeared that there was measured an additive reaction of the acid chloride with benzene, the first rendered active only in so far as it is united to  $\text{AlCl}_3$ , the second rendered active by the total aluminium chloride present.

We have also carried out some measurements with benzene derivatives in order to get some knowledge as to the influence of the substituting group on the reaction velocity; there it was shown that the reaction with toluene using  $N/_{10}$  acid chloride  $\text{AlCl}_3$  at  $30^\circ$  proceeded so rapidly that the conversion had already practically taken place after the mass had become homogeneous, a constant could only be approximated. We give here also the reaction constants for benzene, chlorobenzene, bromobenzene and nitrobenzene at  $30^\circ$  and for a  $N/_{10}$  concentration of the acidchloride- $\text{AlCl}_3$ .

toluene for	0.1 n.	> 0.0064
benzene „	0.2 „	
bromobenzene „		
chlorobenzene „		
nitrobenzene „		
		0.0021
		0.00102
		0.00080
		0.00000

From this little survey we notice that in the reaction of FRIEDEL and CRAFTS, another succession of the velocity influences is observed than in the nitration where, according to the researches of HOLLEMAN and his students, it is exactly opposed to this in the case of the methyl group and the chlorine atom. It may, however, be pointed out that our succession is based on measurements whereas the succession of the nitration is deduced from a comparison of the dirigent power of the groups on the entering nitro-group which, perhaps, has no direct connection with the velocity of nitration.

When carrying out the reaction of FRIEDEL and CRAFTS it is desirable, according to this research, to have the catalyst in small excess when it forms an additional compound with one of the reacting molecules.

*Delft—Wageningen, December 1912.*