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**Chemistry.** — "*The catalyse*". By Prof. J. BÖESEKEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of June 27, 1914).

1. It appears to me that, a summary having been given from various quarters on catalytic phenomena, the time has arrived to show briefly how the development of my ideas on this subject has advanced and how the insight thus gained has been supported by a deduction of one of my students.

I do this in the first place because in that historical account the gradual elucidation of the phenomena is exposed, but also because I imagine that a point has now been reached where the co-operation of many is necessary in order to assist in completing the edifice of the catalysis.

2. When working at my dissertation (1895—1897), when a large number of fatty-aromatic ketones was prepared according to the reaction of FRIEDEL and CRAFTS, it struck me that when to a cooled mixture of acid chloride and benzene finely powdered aluminium chloride was added, this certainly dissolved rapidly, but that an evolution of hydrogen chloride only took place slowly on warming<sup>1</sup>).

As aluminium chloride did not perceptibly dissolve in benzene, I was then convinced that not the benzene but the acid chloride might be the point of attack of the catalyst.

This question was afterwards taken up by me and solved in so far that the synthesis of the aromatic ketones could be divided into two stages: (a) The catalyst combines with the acid chloride: (b) this compound is attacked by the aromatic hydrocarbon (Rec. **19** 19 (1900) **20** 102 (1901).

Although the course of the reaction was indicated therewith, I was soon aware, however, that the *catalytic action* of aluminium chloride remained in complete obscurity<sup>2</sup>).

In this I was corroborated by the observation that chloroform and benzyl chloride suffered the reaction with benzene still far better and more vigorously, whilst these substances did not combine

<sup>1</sup>) Afterwards I modified the preparation by taking the  $\text{AlCl}_3$  in excess and then adding drop by drop the mixture of acid chloride and benzene, because the reaction then proceeded very regularly. By the research of OLIVIER (Dissertation, Delft 1912) it has been shown that the cause of this favourable result must be attributed to the presence of *free*  $\text{AlCl}_3$  (see later).

<sup>2</sup>) PERRIER who had noticed this reaction course previously (Thèse, Caen 1893) was of opinion that this explained the catalytic action of aluminium chloride.

with aluminium chloride and the quantities of the catalyst necessary for the reaction were much less than in the synthesis of the ketones. (Rec. **22**, 301 (1903)).

When it appeared that nitrobenzyl chloride, which *does* unite with  $\text{AlCl}_3$ , was also attacked much less rapidly than benzyl chloride, and further that the very reactive anisol, which also forms a molecular compound with  $\text{AlCl}_3$ , did not react *at all* with  $\text{CCl}_4$ , whereas benzene did so readily, the facts were such that I ventured the thesis that the formation of compounds between the catalyst and the activated substance had nothing to do with the actual catalytic action (Rec. **23**, 104 (1904)) and that, when the catalyst does not unite with one of the substances present in the reaction, we are dealing with catalytic action in its purest form (Rec. **24**, 10 (1905)).

Thus by means of the inductive method, I came to the conclusion that the formation of a compound with the catalyst did not give an explanation of the catalytic action as such, and that with this the theory of the intermediate products exploded.

2. I have also tried to demonstrate subsequently by means of the deductive method that the formation of a compound of substance and catalyst must necessarily lead to a partial paralysis of the latter (Proc. 1907 p. 613; 1909 p. 418).

Hence, if we wished to arrive at a satisfactory explanation this had to be looked for in what happened before there is any question of a compound between catalyst and substance. When the catalyst draws near to the activated substance a phenomenon ought to take place partaking more of a disruption or a dislocation than of a union (Gedenkboek VAN BEMMELEN p. 386, Rec. **29**, 87 (1910)).

I have then demonstrated (Proc. 1909 p. 419; also Rec. **32**, 1 (1913); Chem. Weekbl. **7**, 121 (1910); Rec. **29**, 86 (1910)) that a catalyst like  $\text{AlCl}_3$  exerts indeed a dissociating influence on the chlorides which it activates; chloral was resolved into  $\text{CO}$ ,  $\text{HCl}$  and  $\text{C}_2\text{Cl}_4$ ; trimethylacetyl chloride into carbon-monoxide,  $\text{HCl}$ , and isobutene, etc.

But here it transpired also that even now the explanation was not given, because the action had been too violent; instead of the to be expected condensation products with benzene there were obtained in similar cases, either the decomposition products or the condensation products of these molecule residues with benzene. Thus, from  $\text{SO}_2\text{Cl}_2$  and the benzene hydrocarbons were generated relatively very small quantities of sulphones compared to large quantities of sulphinic acid and chlorine derivatives; owing to too great an activity

the catalyst had disrupted the  $\text{SO}_2\text{Cl}_2$  into  $\text{SO}_2$  and  $\text{Cl}_2$ , which were now subsequently influenced catalytically (Rec. **30**, 381 (1911)).

The catalytic action proper can, therefore, be no union, because in that compound the catalyst is paralysed; it also cannot be a dissociation because the substance is then too much attacked, hence, it must be an intermediary influence.

I have called the latter a *dislocation* or *disruption* (Rec **30**, 88 (1911) dating from Sept. 1909) in order to demonstrate that there certainly does exist an influence, but that this should effect neither union or dissociation if it is to be considered as a purely catalytic one. In order to more sharply confirm experimentally this result obtained, the transformation of chloral into metachloral under the influence of diverse catalysts was submitted to a closer investigation. <sup>1)</sup>

This system was chosen because it had been shown that:

1<sup>st</sup> it is an equilibrium between two substances, therefore a very simple case because we are only dealing with the transformation of one substance into another one.

2<sup>nd</sup> this equilibrium is situated in a readily attainable temperature-zone, whereas the properties of monomeride and polymeride differ rather strongly, so that the specific influence of the catalyst may come perceptibly to the fore.

3<sup>rd</sup> That the monomeride itself is a supercharged molecule, so that it was to be expected that the action of the catalyst would be a pronounced one.

In fact it could now be demonstrated that the equilibrium was attained rapidly only then when the activator was present in small quantities and had not perceptibly united with one of the modifications.

If the catalyst (pyridine) was retained (absorbed) in the colloidal polymeride the equilibrium set in, but in the liquid phase of the monomeride the reaction ceased.

If the catalyst combined with one of the components (the monomeride) the equilibrium was shifted in the direction of that component.

If, finally, the action of the activator was stronger still, the splitting products were obtained only.

About the same time, S. C. J. OLIVIER (Diss. Delft 1913, Proc. 1912 and R **33**, 91 (1914) had finished a dynamic research on the action of bromobenzenesulphochloride on some benzene-hydrocarbons under the influence of aluminium chloride.

Whereas the researches had been as yet of a qualitative character it could now also be demonstrated quantitatively that the retention

<sup>1)</sup> R **32**, 112 (1913).

of the catalyst in the sulpho-chloride or in the sulphone caused a partial paralysis, as the reaction proceeded much more rapidly the moment a small quantity of the catalyst in the solution was present in the free state.

Also, could it be deduced sharply from the progress of the reaction (Proc. 1913 p. 1069) that this could be explained satisfactorily only then when the activating action was sought in what happened between benzene on one side and chloride + catalyst on the other side before they had undergone chemical transformation.

Hence, it was proved experimentally also here that the most important stage of the catalysis is that which takes place before the union.

3. If we now consider what can be the significance of the removal of the catalysis to the pre-stage of the reaction, it should be remembered that in view of OSTWALD'S definition a catalyst should be a substance unchanged in quantity and quality after the reaction.

Guided by this definition we may *during the reaction* assume all kinds of material and energetic changes if only the condition is satisfied that the catalyst remains unmodified before the beginning and after the end of the reaction.

If now, however, we look for a further explanation, that is to say, penetrate further into the mechanism of a reaction, we notice that somewhere during the reaction a catalyst can no longer satisfy that definition.

Hence, a catalyst can never remain unchanged during the entire course of the reaction; an ideal catalyst exists no more than an ideal gas or an ideal dilute solution, but for all that we have been able to make excellent use of the notion.

Now, a substance will approach this ideal condition all the more, the smaller the material or energetic displacements will be and it is plain without any further evidence, that similar very small changes will just take place on the approach of the catalyst to the bonds to be activated.

When there the action ceases, we can understand that these shiftings may be so small that they elude observation (so that for instance, apparently a *same* equilibrium is reached under the influence of *diverse* catalysts, which in reality cannot be the case.)

4. If now we want to get a concrete conception of these exceedingly small actions, which in the catalysis are both satisfactory and authoritative, we may consult the modern views on our atomic world.

It is supposed that the atoms consist of (or at least are populated by) electrons and that they hold together by means of force regions between these corpuscles; the catalytic action may then be described as a change of these force regions on the approach of the catalyst. If this is so, we have in the *pure* photocatalysis the simplest catalytic actions and the study of these phenomena will no doubt much deepen our insights.<sup>1)</sup>

On penetrating further into the phenomena in general we are obliged to resolve the substance into steadily decreasing units and the same has happened with the special phenomena called catalytic; here it will just be shown that what takes place in the atoms will be of preponderating importance. But just as we have not been able to find the ideal catalyst among the atoms, we cannot expect to meet it among the electro-magnetic equilibria-perturbations, only the limit of our insight in the catalytic phenomena has advanced a step.

## II.

1. During this mainly inductive development of my ideas my pupil H. J. PRINS had found a synthesis of chloropropane derivatives and I advised him to couple this experimental subject with a survey of the different cases in the reaction of FRIEDEL and CRAFTS.<sup>2)</sup>

With this, however, he did not content himself, but starting from the "Principle of Reciprocity" he has endeavoured to furnish an explanation of the catalytic phenomena in general, with the reaction of FRIEDEL and CRAFTS as a special case.

The result of this is given in his dissertation ("Bijdrage tot de kennis der katalyse", Delft 1912) and supplemented with a few subsequent articles (Journ. f. pr. Chem. N. F. **89**, 425 (1914); Chem. Weekbl. **11**, 474 (1914)).

In order to reproduce PRINS's intention in the simplest possible manner, I will quote a few parts of his deduction, taking the liberty to omit the, in my opinion, non-essential matter.

<sup>1)</sup> The simplest case is the photocatalytic change of a monatomic element.

<sup>2)</sup> The reaction of FR. and CR. offers us already a great diversity of catalytic reactions, because  $AlCl_3$  can form all kinds of compounds. Only in such cases where it unites neither with the initial products nor with the end product, or attacks this secondarily do we approach a case of pure catalysis.

The number of these cases is very small, the chlorination of benzene is a very appropriate example thereof; here the quantity of the catalyst is minimal indeed (see further).

The axioms which are more particularly applicable to the catalysis are :

“When... the one exerts an influence on the other, this latter... is changed by the first...”

“If in the calculation of one of these the change may be neglected we may speak of a one-sided influencing, which, however, as such... may not be considered one-sidedly (dissertation p. 4—5).

and subsequently :

“If we consider the possible relation of two substances (whether element or compound) three stages are to be distinguished therein”.

“1. The stage of the relative inertness. In this stadium even the catalytic influence is imperceptible, whilst there is no question of a chemical compound.

“2. The catalytic stage<sup>1)</sup> in which occurs also the mutual activation. In this stage the catalytic actions are enacted.

“3. The reaction stage in which appears an intra- or extra-molecular reaction”.

The catalytic stage forms the bridge between the inertness and the chemical compound. In each chemical reaction all three stages are gone through.

By varying the conditions we can, however, cause the influencing to be confined to the second stage”. (Chem. Weekbl. **11**, 475, also Journ. f. pr. Chem. N. F. **89**, 448 (1913).

2. PRINS starts from the general thesis that on interaction, there takes place a change in two conditions, which will be least powerful the moment it begins to reveal itself.

This stage lies, chemically speaking, in the dissociation region where the free energy of the entire system approaches to zero and is called by PRINS the catalytic stage.

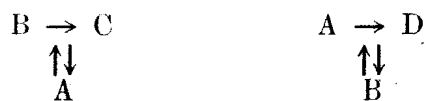
In this catalytic stage there is really no question of a catalyst in the sense of OSTWALD; we are dealing with a change of condition:  $A \rightleftharpoons B$  which taken by itself can take place more or less rapidly.

Being in the catalytic stage does not at all imply, in my opinion, that the changes must take place rapidly; this depends on the nature of the change (chemically speaking on the nature of the atoms or atomic groups which in the transformation play a role in the first place).

If, for convenience sake, we call A and B two molecules, one of these molecules, in a reaction in which the other one (with its

<sup>1)</sup> In order to prevent confusion it would be better to speak of the activating stage. (PRINS also points out that the word “activator” expresses his ideas better than catalyst).

specific atomic group) occurs as a component, will be a catalyst in the sense of OSTWALD.



The above symbols represent this explanation from which we gather that the change of the free energy in so far as it concerns the catalyst approaches in the pure catalysis to zero and wherewith we also wish to express that the catalyst is in fact more a change of condition than a substance.

In the positive catalytic action the equilibrium  $A \rightleftharpoons B$  will set in much more rapidly than the reaction  $B \rightarrow C$  or  $A \rightarrow D$  and thus cause or accelerate the same.

Hence an ideal catalyst, according to this deduction and in connexion with OSTWALD's definition, is a substance which undergoes with one of the to be activated substances (or bonds) such reciprocal action that in the latter system the thermodynamic potential and chemical resistance simultaneously approach to zero.

As it concerns here particularly the bond that is being activated, the other molecule will also be more or less influenced; this we notice immediately when we remember that intramolecular displacements come under the same point of view.

Hence, we will obtain the maximal catalytic action when, with the catalyst (for instance B) we approach as closely as possible the catalytic stage in regard to A as well as D.

The chlorination of benzene again presents us with a suitable meaning example to elucidate the intention of this thesis.

Both chlorine and benzene are in regard to  $AlCl_3$  in the catalytic stage; they are both rendered active without forming a compound.

As soon as we replace benzene by nitrobenzene the action ceases at the ordinary temperature because  $AlCl_3$  forms a solid combination with nitrobenzene so that these two are, in regard to each other, not in the catalytic stage and because  $AlCl_3$  cannot any longer activate the chlorine simultaneously.

At a higher temperature the chlorination starts; we may assume that the system  $AlCl_3, NO_2, C_6H_5$  is then again approaching the catalytic stage.

It is, however, self-evident that a case like the chlorination of benzene is rarely met with; as presumably somewhat similar cases I mention: all ionreactions in aqueous solutions; the union of hydrogen and oxygen and the decomposition of hydrogen peroxide.



on or in platinum; the transformation: aldehyde = paraldehyde under the influence of sulphuric acid etc.

Much more frequent will be the cases, such as in the chlorination of nitrobenzene, where the catalyst is found, in regard to one of the substances, a good long way over this most favourable stage; in that case it will have united with one of the components to a more or less firm compound.

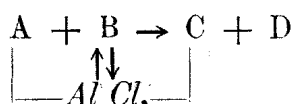
The sulphone formation from bromosulphone-chloride and benzene under co-operation of  $AlCl_3$  is an illustrative instance hereof:

The  $AlCl_3$  is combined with the sulphone-chloride and is, therefore, in regard to the chloride, already far removed from the catalytic stage, at  $25^\circ$  it is however not completely paralysed, as according to the course of the reaction it is still capable of activating the second molecule (benzene).

The sulphone formed now also unites with  $AlCl_3$  and now it appears also from the course of the reaction that it keeps on activating the benzene, but is, however, no longer capable of influencing the sulfone-chloride, for an excess of the latter exerts no influence on the reaction velocity. (OLIVIER and BÖSEKEN, Proc. 1913 l. c.).

From this case it is shown how complicated this reaction may become when in the reaction mixture different substances are present which paralyse the catalyst more or less, and that only a clear conception of the catalysis enables us to interpret the observations satisfactorily.

Represented symbolically, we thus have here (when we assume that the  $HCl(D)$  does not interfere, which has also been proved by OLIVIER):



The  $AlCl_3$  united to  $C$  (the sulphone) can no longer reach  $A$  (the sulphonechloride), only the  $AlCl_3$  united to  $A$  itself can still activate the  $S-Cl$  bond, but much less so than free  $AlCl_3$ ; only the benzene ( $B$ ) is still attainable for the  $AlCl_3$ .

I want to observe here that the paralysis starts here, presumably, from the  $SO_2$ -group, because this occurs in the sulphonechloride as well as in the sulphone.

These are just the cases, wherein the catalyst is united with one of the starting products, but is not entirely paralysed thereby, which have originated the theory of the intermediate products.

By removing wilfully from the most favourable catalytic stage

(for instance by lowering the temperature) similar compounds have often been met with and it was imagined that the explanation of the catalytic phenomena had thus been found.

Now, however, it is evident that the explanation is not given by the formation of these compounds, but should be found *before* the formation and that the best catalysts will be those whose dissociation equilibrium extends over as large as possible a region of temperature and pressure, without any compounds being formed.

3. In this manner, ascending by the inductive method from the special case of the reaction of FRIEDEL and CRAFTS (BÖESEKEN) and descending by the deductive method from the general principle of reciprocity (H. J. PRINS), we have come to the conclusion that the catalytic action is situated in the pre-stage of the chemical union.

It is evident that with this result no explanation has been found in the sense that now everything is completely elucidated.

Yet, in my opinion, owing to the sharper definition of the conceptions the whole field is easier to survey (PRINS l.c.) and the special cases are more readily understood, also a fundament has been given on which we can pursue our researches with a greater certainty.

These in view of the further elucidation will have to move in two directions.

1<sup>st</sup>. It must be ascertained, as has been already done in some cases (l.c.), in how far the change in velocity is connected with the shifting of the catalyst and activated bonds in the dissociation region.

With this may be coupled systematic researches as to the most suitable catalysts for specified reactions, (for instance on metals which are in a rapidly setting in dissociation-equilibrium simultaneously with  $N_2$  and  $H_2$  at a low temperature in view of the ammonia synthesis; or on carbonates which in view of the ketone synthesis from acids according to SABATIER and SENDERENS must, at about  $300^\circ$ , be with those acids in the same favourable conditions).

2<sup>nd</sup>. Those catalytic actions must be investigated where very small energy shiftings are concerned; to this appertain in the first place the photocatalytic phenomena.

The first series of researches are of a more direct practical result; the second series, on the other hand, are of a more penetrating nature, the object being to attack the catalytic phenomena in their last recess.

*Delft, June 1914.*