ON THE INDUCED REACTION.

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Since an observation regarding the induced reaction appeared in Mohr's text-book (1855), many chemists have treated it, but its theory still remains unknown. Further, the induced reactions so far described appear to be limited to oxidation reactions, and they are called induced oxidation in other words.

The writer, in the course of a study of isomerization of eugenol and safrol, has discovered an induced reaction, which differs in its nature from any known before, and he has shown it to be a kind of catalytic action.(1)

For the isomerization of safrol into isosafrol, caustic potash is usually used as catalyst, heat being applied at the same time. But, eugenol is difficulty isomerized by the same treatment and gives sometimes a resinous matter, but the reaction generally does not take place. On the other hand, if, eugenol is mixed with safrol and treated with caustic potash as in the case of safrol transformation, eugenol is smoothly isomerized into isoeugenol, safrol being transformed into isosafrol at the same time. Further, experiments have shown that when eugenol and safrol are mixed together, not only eugenol but also safrol are completely isomerized at such a low temperature as would not cause the formation of isosafrol if safrol exists alone. The isomerization of eugenol may be considered to become easy owing to any one of the three following causes : (1) either safrol or isosafrol is a suitable solvent for eugenol ; (2) either safrol or isosafrol catalytically accelerates the isomerization of eugenol ; (3) the isomerization of safrol induces the isomerization of eugenol.

In order to ascertain which one of these was the real cause, the writer used various solvents as substitutes for safrol, but no positive result was obtained. Even if isosafrol was used as the solvent, the result was negative. It could not be considered that eugenol isomerization was due to the catalytic action of safrol, because safrol becomes isosafrol promptly. Therefore, for the explanation of eugenol isomerization it must be considered that the isomerization of eugenol is accelerated by the isomerization of safrol in the presence of caustic potash ; in other words this phenomenon is an induced reaction, where the primary reaction with safrol as inducer and caustic potash as actor accelerates the reaction of caustic potash and eugenol as

(1) *J. Chem. Soc. Japan*, **45** (1924), 209.

acceptor. This view has naturally extended the induced reaction to isomerization beyond oxidation.

A very interesting fact is that, irrespective of the quantity of safrol, and thus in spite of much smaller quantity of safrol compared with that of eugenol, the latter isomerizes vigorously. Not a few authors have explained the mechanism of the induced reaction as consecutive reaction ; but, taking into account such views as that of Mellor[2] represented by the formula

$$\text{Induction factor} = \frac{\text{Amount of acceptor transformed}}{\text{Amount of inducer transformed}},$$

it is possible to increase the induction factor to a very large quantity, and the experimental results of the writer have evidently verified that this induced reaction is a catalysis.

The writer, desiring further to extend the above theory to general reactions, has obtained another example.[3] Diphenyl oxide is formed in the reaction expressed by the following equation, copper powder being used as a catalyst:

$$C_6H_5OK + C_6H_5Br = C_6H_5OC_6H_5 + KBr.$$

In case sodium phenolate is used instead of potassium phenolate, the reaction velocity is extremely reduced, but if potassium phenolate and sodium phenolate are mixed together, the reaction proceeds more rapidly than when they are used separately, just in the same manner as the mixture of safrol and eugenol is isomerized by caustic potash.

For such an induced reaction, the writer proposes the name " mutually induced reaction ". He considers that, in this case, the relation of the primary reaction to the secondary will be just the same as the relation of the secondary to the primary, each accelerating and promoting the other.

Besides, the writer has given elsewhere many examples of induced reactions and verified that they are all mutually induced reactions.[4] A list of examples including the above-mentioned is given in Table 1.

Table 1.

Primary reaction	Secondary reaction	Actor	Inducer	Acceptor
Safrol+KOH	Eugenol+KOH	KOH	Safrol	Eugenol
Eugenol+KOH	Safrol+KOH	KOH	Eugenol	Safrol
KOH+Eugenol	NaOH+Eugenol	Eugenol	KOH	NaOH
KOH+Safrol	NaOH+Safrol	Safrol	KOH	NaOH
$C_6H_5OK+C_6H_5Br$	$C_6H_5ONa+C_6H_5Br$	C_6H_5Br	C_6H_5OK	C_6H_5ONa

(2) " Chemical Statics and Dynamics ", (1904), 333.

(3) *J. Chem. Soc. Japan,* **47** (1926), 368.

(4) *J. Chem. Soc. Japan,* **47** (1926), 357 ; *ibid.,* **48** (1927), 171.

As given in the table, in these induced reactions, the constitutions and chemical properties of the inducer and the acceptor resemble each other. In view of these facts, the writer has made further experiments by mixing substances of similar constitutions and has obtained an unexpected result of an induced reaction.(5) By the action of dilute sulphuric acid citronellal produces a large quantity of isopulegol, while citral, a minute quantity of dehydroisopulegol. The writer has, therefore, treated the mixture of these two substances in the same way with the expectation that, by induction, these two alcohols might be formed in larger quantities ; but, on the contrary the reaction proceeded to an entirely different direction, and each formed a pinacone. These pinacones have not yet been recorded and the writer named them dicitronellal pinacone, $(C_{10}H_{17})_2(OH)_2$, and dicitral pinacone, $(C_{10}H_{15})_2(OH)_2$, respectively. They are formed in large quantities in the above reaction, which affords a good example of the formation of two similar substances from two other similar substances.

To sum up, the induced reaction is explained by the writer in the following manner. When two homologous substances or substances of similar structures are mixed, they catalyze each other, and similar reactions always take place. If one of the two substances reacts with a third substance, they act as inducer and acceptor to each other, and this action accelerates the reaction to a further extent and thus causes induction. In other words, in these induced reactions, the fundamental condition is that the inducer and the acceptor must have a resemblance in chemical structure and properties.

Having found such a fundamental feature of the induced reaction, the writer has made an observation in some usual catalytic actions. As shown in Table 1 the isomerization of eugenol is an induced reaction, in which caustic potash and caustic soda mutually act as inducer and acceptor, but this induced reaction may be described as a catalytic action with caustic soda as catalyst and caustic potash as promotor. Consequently, an induced reaction of this kind is nothing but a catalysis with a promotor. With this view, the writer has investigated the reactions formerly considered mere promotor reactions and found an interesting fact. For instance, it is known that in the ammonia synthesis catalyzed by iron, if molybdenum, tungsten, uranium, etc. are used as promotor, the catalystic activity of iron increases, thus accelerating the velocity of the formation of ammonia. In the case of formation of hydrogen from water gas, $CO+H_2O = CO_2+H_2$, the velocity of formation is said to be greater if the oxides of nickel, chromium, etc. are used as promotor with iron catalyst than if iron alone is used. Further, in the case of producing aniline black from aniline, *p*-diamine or *p*-aminophenol is

(5) *Ibid.*, **47** (1926), 417.

used with vanadium salt as catalyst. In the two former instances, the resemblance in the properties between the catalyst and the promotor is quite clear from the periodic system. In the last instance, although the promotor does not resemble the catalyst, it possesses properties similar to those of aniline, the subject of the reaction.

If the above examples are considered in the light of the writer's opinion that two similar substances mutually act as inducer and acceptor on each other and can cause an induced reaction, it is conceivable that these promotor reactions can also be described as induced reactions.

The writer wishes to extend the observation to catalytic actions in general. The above-described induced formation of diphenyl oxide is conceivable as a reaction of sodium phenolate and bromobenzene catalyzed by potassium phenolate. Or again, the isomerization of eugenol, if this be described as a reaction of eugenol and sodium hydroxide, may be said to be a catalysis by potassium hydroxide. Thus, these induced reactions may be considered as ordinary catalytic actions.

The formation of dicitronellal pinacone appears to be slightly different from the above. As a rule, citronellal yields isopulegol in the reaction with sulphuric acid, but, when it is mixed with citral, the formation of isopulegol is retarded exceedingly, and on the other hand, the reaction is directed toward the formation of dicitronellal pinacone which induces the formation of dicitral pinacone. If this induced reaction is considered a catalytic action by citral, then citral acts poisonously on the formation of isopulegol, that is to say, as a negative catalyst. Consequently, the induced reaction given above involves not only positive but also negative catalysis.

These explanations will show that many examples of catalytic actions, whether positive or negative, and of promotor actions can be described as induced reactions in the sense defined by the writer, that is, reactions taking place when two similar substances are mixed together.

How can the mechanism of this new and particular induced reaction be explained? The radiation theory of reactions proposed by Perrin or C. W. Lewis was once valued as an interesting hypothesis, but the experiments do not support it. If the radiation theory is applied to the present case, it appears that the explanation may be given easily on the basis that the particular radiation emitted by the primary reaction has induced the secondary reaction. However, in this case also, there is no experimental fact to support the hypothesis. Furthermore, the fact that the induction factor can be enlarged to infinity brings about the difficulty that the induced reaction must be considered as a photo-chemical chain reaction. These facts lead the writer to the consideration that this catalytic action may be solved by the collision theory with the special steric factor taken into account. The writer will further make quantitative experiments and desires to study carefully the mechanism.

At any rate, in view of chemical synthesis, this induction may be utilized to accelerate the reaction velocity ; or in the absence of any known standard for the choice of a catalyst, a consideration of the induction may now give some suggestions for this purpose.

Summary.

(1) The induced reaction, which was formerly limited to oxidation reaction, has been extended to reactions in general, and many examples have been given.

(2) All these induced reactions have been proved to be catalytic actions.

(3) Evidences have been given to show that among catalytic actions, positive or negative, and promotor actions, there are many instances which can be described as induced reactions.

(4) It has been shown that these induced reactions must always have two similar substances as inducer and acceptor.

The above thesis is based upon many experiments made since 1924 under the guidance of Dr. Matui, President of the Imperial University of Kyoto. The writer has also been given many valuable advices by Prof. Horiba. He wishes to express his hearty thanks to them.

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