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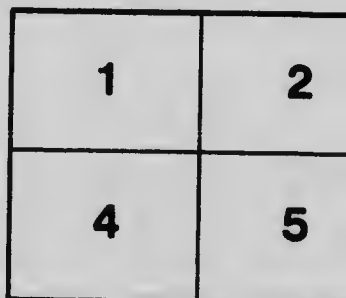
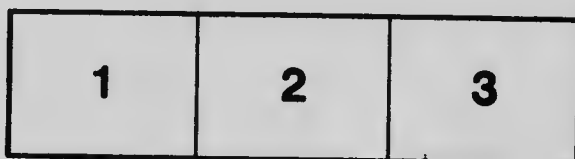
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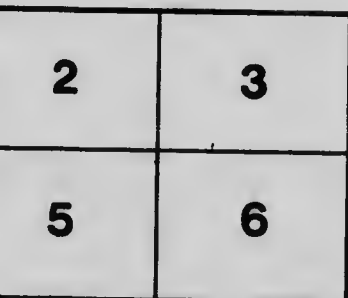
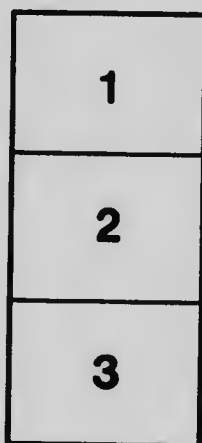
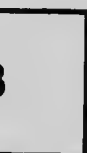
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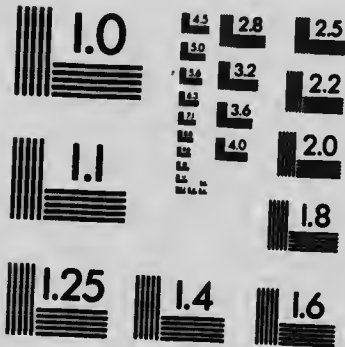
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ON THE MECHANISM OF INDUCED REACTIONS

BY W. LASH MILLER

The word "Induction," in the sense in which it is used in this article, was introduced into the chemical literature by F. Kessler, in 1863.

"Let $R\alpha$ and $R\beta$ be two reducing agents" (with $O\alpha$ and $O\beta$ two oxidizing agents, such that under the same conditions $R\alpha$ reacts easily with $O\alpha$ while $R\beta$ and $O\alpha$ react with difficulty or not at all. If then, on bringing all factors together under these conditions, we find that the reaction between $R\beta$ and $O\beta$ is accelerated, we will regard this as "induced" by that taking place between $R\alpha$ and $O\alpha$. In most cases, at least so far as my knowledge goes, the former case is specialized, either by $O\alpha$ being identical with $O\beta$ or $R\alpha$ with $R\beta$. To distinguish these two cases, the former "induced oxidation" and the latter "induced reduction."

A large number of experimental and theoretical papers dealing with the subject of chemical induction have appeared since Kessler's time; lists are given by Manchot,¹ Weissberg,² Schirow,³ Luther,⁴ and Mellor.⁵

The term "induced reaction" is now generally applied to Kessler's special case, in which only one oxidizing and two reducing agents are present or *vice-versa*. The term "actor" is given to the oxidizing agent in cases of induced oxidation, and to the reducing agent in cases of induced reduction. The "inductor" is the substance which reacts with the actor, and accelerates or "induces" the reaction.

¹ Pogg. Ann., 119, 218 (1863).

² Liebig's Ann., 325 (1902).

³ Kritische Studien über die Autoxydationsvorgänge, Leipzig, 1903.

⁴ Zeit. phys. Chem., 42, 641 (1903).

⁵ Ibid., 46, 777 (1903).

⁶ Chemical Statics and Dynamics, London, 1904.

INDUCED REACTIONS

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the chemical vocabulary

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actor and the third reagent, or "acceptor." The "induction factor" gives the number of equivalents of acceptor which enter into reaction while one equivalent of inductor is oxidized (or reduced) by the actor.

From the theoretical point of view, the simplest cases that come under Kessler's definition are those in which the induction can be explained by the known properties of an isolable product of the reaction between actor and inductor. In order to make sure that the explanation suggested is the true one, it is only necessary to study the two reactions: actor *plus* inductor, and product *plus* acceptor, separately, and compare them with the reaction which takes place in solutions containing actor, inductor, and acceptor together. This has been done by Harcourt and Esson¹ and by Bell² for the system H_2O_2 , HI, $Na_2S_2O_3$; by Federlin³ for the system $K_2S_2O_8$, HI, H_3PO_3 ; by Schilow⁴ for the system $HBrO_3$, HBr, $HAsO_3$; and by Bowman⁵ for the system $HBrO_3$, HI, $HAsO_3$. Cases like these belong demonstrably to the group of consecutive reactions, none of which were included by Kessler in his tables of examples; and it seems better to employ the term "induced reaction" only where no such obvious explanation is available.

It is possible, of course, to account for the remaining cases by assuming the temporary existence of some product which could take the place of the iodine or bromine in the foregoing examples, even where all attempts to isolate such a substance have failed. The first attempt to carry this idea through in detail was made by Mauchot, whose views may be gained from the following much abridged free translation from his papers "On the Process of Oxidation"⁶ and "On the Formation of Peroxides of Iron,"⁷ published in 1902.

¹ Jour. Chem. Soc., 20, 476 (1867).

² Jour. Phys. Chem., 7, 61 (1903).

³ Zeit. phys. Chem., 41, 565 (1902).

⁴ Ibid., 42, 641 (1903).

⁵ The results of this research will shortly be published.

⁶ Liebig's Ann., 325, 93 (1902).

⁷ Ibid., 325, 105 (1902).

Manchot's Peroxide Theory

"I was led to the following general theory of the processes of oxidation, which is completely contained in the sentence " *In every process of oxidation there is formed a primary oxide*¹ which in general has the character of a peroxide. The subsequent fate of the peroxide depends on the special circumstances of each case. The case that the final, isolable, product is identical with the peroxide seems to be the less common . . . it is more usual for the peroxide to undergo decomposition before it can be isolated, giving up oxygen, which escapes as gas, or combines with other substances present (acceptors); among the latter may be included the substance itself which is undergoing oxidation (auto-acceptor).

" *The peroxide is formed direct from the reagents, intermediate states are passed over . . .* and it is obviously only in special cases that the isolable product is more highly oxidized than the initial state (c. g., ferrous-peroxide-ferric). The final state may be identical with the initial, or may be less oxidized than the latter, for instance the reduction of PbO_2 or MnO_2 by H_2O_2 in presence of acid (dioxide-peroxide-monoxide) . . . and in some cases the product of decomposition may be the metal itself (Au from AuCl_3 by H_2O_2 , etc.).

"This theory necessitates the assumption in the case of many elements, of stages of oxidation which are hitherto unknown. . . . It brings the action of all oxidizing agents under a common point of view, but I wish to state emphatically that in my opinion it is of value chiefly because it incites to experimental investigation, and, without predicting the results of the latter, is able to modify itself in accordance with them. If in any case this should clearly be shown to be impossible, the theory must be laid aside."

Granting that the "primary product" of the oxidation of ferrous sulphate, for instance, is a peroxide of iron, the composition of the latter may be ascertained "by carrying

¹ The italics are the author's, throughout.

out the oxidation in presence of an acceptor, to which oxygen may be transferred from the peroxide. Many substances can act as acceptors, but for quantitative investigations only those of them are suitable which react fairly quickly with the ferric peroxide, so that the reduction of the peroxide is brought about *only* by the acceptor, the evolution of oxygen, or its transference to other substances (especially unused ferrous salt) being avoided. The action of the peroxide on the acceptor may be rendered more complete by increasing the concentration of the latter."

When a suitable acceptor has been found, it is only necessary to determine n , the number of atoms of oxygen absorbed by the acceptor for every Fe_2O_2 converted into Fe_2O_3 ; for the formula of the peroxide may be assumed to be $\text{Fe}_2\text{O}_{3-n}$.



Thus, according to Manchot, every process of oxidation leads to the formation of a primary oxide, which in general has the character of a peroxide, and whose formula may be ascertained by determining the induction factor.

Luther and Schilow's Classification

Luther and Schilow¹ take a much broader view, and admit the existence of many types of induced reactions.

They begin by distinguishing cases of simple catalysis under conditions where the catalyzer is destroyed by independent reaction with the actor from true copulated reactions; in the former the induction factor can be increased indefinitely by increasing the concentration of the acceptor; in the latter it reaches a limit which depends on the nature of the reaction "really" taking place in the solution.

The authors then discuss "the main question, namely, the methods of ascertaining the nature of the intermediate substance which brings about the copulation."

The upper limit, towards which the induction factor

¹ Zeit. phys. Chem., 46, 777 (1903).

tends as the concentration of the acceptor is increased, may be employed to determine the degree of oxidation of the intermediate compound, but gives no further information as to its formula, or as to the reagents from which it has been formed. In the authors' opinion, information on this point "can be obtained only by *suitable variation of the reagents*; reagents which are necessary for the formation of the intermediate substance must have certain properties, so that they can be varied (interchanged) only within definite limits; substances which can replace one another must in certain respects be *chemically analogous*, or at least be capable of *analogous chemical changes*. On the other hand, the substances which only react with the intermediate body may belong to widely different chemical classes, the single respect in which they must resemble one another being their ability to enter into an oxidation-reduction reaction with the (hypothetical) intermediate substance."

"Observation of the occurrence or non-occurrence of induction, when the reagents are systematically varied, therefore enables one—to a certain extent—to decide which of these substances plays a *specific rôle* in the reaction and leads to a classification of the cases of induction hitherto observed. The principle underlying the following attempt at such a classification, is the dependence of copulation on the specific nature of the three reagents—actor, inductor, acceptor."

In class A, the inductor is "specific," the other two "unspecific;" the intermediate body must therefore be a derivative of the inductor; in classes B and C, actor and acceptor respectively take the place of the inductor of class A. In class D, both acceptor and inductor are "specific," and the intermediate body must be regarded as a complex derived from both of them; classes E and F complete the series, inductor and actor, or acceptor and actor respectively, being "specific."

In the authors' attempt to distribute the known cases of induction among their six classes, the weakness of the "prin-

ciple" on which the classification rests becomes apparent. Ferrous salts, for instance, act as inductors in 15 reactions involving 7 actors and 9 acceptors—all are grouped in class A; but the 8 reactions in which SO_2 takes the part of inductor, and in which 6 actors and 4 acceptors are involved, are distributed among the remaining five classes. "This example shows how careful one must be in interpreting the phenomena of induction;" it also shows that much is left to individual opinion in the practical application of the authors' "principle" of classification; Luther and Schilow were quite clear on this point, "we consider our interpretations as in no case final."

A New Classification Based on Kinetic Measurements

A firmer basis for the classification may be secured by treating the problems of induction according to the methods of chemical kinetics; and comparing the rates at which the actor acts on inductor and acceptor taken each by itself, with the rates in solutions containing all three reagents together. Each case, of course, must be studied by itself, but when the effects of all the concentrations on the rates have been ascertained, a suitable hypothesis may be founded on the results of the measurements.

In the present almost total absence of experimental data, it would be premature to develop a detailed classification of the results that may be attained by future experimenters; it is sufficient to define the three classes into which all must fall, and to attract attention to an important ambiguity that must always attend attempts to assign a specific mechanism to any case of induction which falls under group II of the classification proposed.

The Three Classes

It is assumed that in every case the final products of the reactions in solutions containing all three reagents, are the same as the products of the reactions between actor and acceptor or actor and inductor separately. This excludes the obviously consecutive reactions referred to on page 10.

Class i.—The rate at which the inductor is acted on. and

the influence of the concentrations of the reagents on that rate, are unaffected by the presence and concentration of the acceptor. The reaction comes under the head of "Catalysis combined with destruction of the catalyzer," and as pointed out by Luther (page 12) the induction factor rises indefinitely with increase in concentration of the acceptor.

Class ii.—The rate at which the actor is destroyed, and the influence of the concentrations of the reagents on that rate, are independent of the presence and concentration of the acceptor; while the rate at which the inductor is acted on, though (necessarily) slower than in absence of the acceptor, is nevertheless affected by the concentrations of the reagents in the same manner as in the absence of the acceptor. The induction may be accounted for by assuming one of Manchot's peroxides or some other product of the action of actor on inductor. This is the only case which the peroxide hypothesis is sufficient to explain; it includes Luther's classes A, B and E.

Class iii.—The effect of the concentrations of the reagents on the rate at which the inductor is destroyed is changed by adding the acceptor. The intermediate formation of some derivative of the acceptor with actor or inductor may be assumed (Luther's D and F), or resort may be had to complicated hypotheses involving equilibria; the peroxide explanation, however, is clearly excluded.

The difficulties met with in carrying out the measurements necessary for this classification are principally those of chemical analysis: up to the present, however, only two cases of induction have been studied from this point of view, *viz.*: those in which the action of chromic acid on potassium iodide is accelerated by the simultaneous oxidation of ferrous sulphate or of arsenious acid, respectively. They afford typical examples of classes iii and ii.

Chromic Acid, Ferrous Sulphate, Potassium Iodide. Type of Class iii

This reaction is particularly interesting as it is one of those discussed by Manchot, who thought it afforded striking

evidence of the correctness of his theory. He considered the "primary product" of the reaction between chromic acid and ferrous sulphate to be a peroxide of the formula Fe_2O_6 , which was instantaneously reduced to ferric oxide or its salts by the action of ferrous salts or of iodides. As this theory, which was subsequently adopted by Luther and Schilow, is totally at variance with the results of the kinetic measurements quoted below, it is worth while to recapitulate the arguments advanced in its support.

Manchot relied on his general theory of oxidation, outlined above (page 11), and on the observation that there is a "slight but distinct evolution of oxygen gas when ferrous sulphate is dropped into a concentrated solution of potassium bichromate in sulphuric acid;" he arrived at the formula of the peroxide by means of the induction factor. Theories of the induction based on a hypothetical ferro-hydriodic acid he dismissed on the ground that "potassium ferrocyanide¹ added to the system: chromic acid *plus* hydriodic acid, produces the same effect as ferrous sulphate, namely, sets iodine free; the liberation of iodine takes place a little more slowly, probably because the peroxide is more stable in this case; obviously there can be no talk of the formation of a ferro-hydriodic acid in this case, nor of similar complexes in the experiment on the decolorization of indigo, described below."

The considerations weighing with Luther and Schilow may be put shortly as follows. Ferrous salts act as inductors in numerous reactions involving actors and acceptors of the most varied character; these cases, therefore, all come under Group A (page 13), and are to be explained by assuming the primary formation of "an intermediate state of the inductor," that is, a peroxide of iron.

Miss Benson's measurements,² however, show that the effect of the concentrations of the reagents on the rate at which ferrous sulphate is oxidized by chromic acid are altogether

¹ See, however, Miss Benson's measurements: Jour. Phys. Chem., 7, 363 (1903).

² Jour. Phys. Chem., 7, 356 (1903).

changed by the addition of potassium iodide. In the absence of potassium iodide the rate is proportional to the square of the concentration of the ferrous salt, in its presence to the first power; in the absence of potassium iodide, to the second power of the concentration of the acid, in its presence, to the third or fourth power; in the absence of potassium iodide to the 1.4th or 1.8th power of the concentration of the bichromate, in its presence to the first power, while the effect of continuously increasing the concentration of the iodide is first to lower, then to increase the rate at which the ferrous sulphate was oxidized.

The case therefore comes under Class iii of page 15; and *it is quite impossible to assume, with Manchot, and with Luther and Schilow, that the reaction between ferrous sulphate and chromic acid in the presence of potassium iodide is essentially the same as in its absence.*

Chromic Acid, Arsenious Acid, Potassium Iodide. Type of Class ii

This reaction is not included in Luther and Schilow's tables, and is not mentioned by Manchot; the kinetic investigation, which has been carried out by Mr. R. E. Lury,¹ establishes it as the type of Class ii.

Whether potassium iodide be present or not, the rate at which arsenious acid is oxidized by chromic acid is proportional to the concentrations of the arsenious acid and bichromate, and to the 1.4th power of that of the acid. When potassium iodide is added, iodine is set free; and as the concentration of the iodide is increased the rate of liberation of iodide increases and the rate of oxidation of arsenious acid decreases, until the latter falls to one-third the rate in the absence of iodide. When this point has been reached, two equivalents of iodine are liberated for each equivalent of arsenious acid oxidized, and further increase in the concentration of the iodide has no effect on the rates. Throughout, the rate at which the chromic acid is reduced by the mixture

¹ Trans. Roy. Soc., Canada, May, 1905.

of iodide and arsenious acid is the same as though the arsenious acid were present alone.

Thus, in contrast to the case of induction studied by Miss Benson, *the reaction involving the reduction of chromic acid is essentially the same whether iodide be added or not*; it may therefore be accounted for by assuming that a (hypothetical) peroxide of arsenic is the primary product of the reaction whose rate is measured, and that this peroxide is immediately reduced to arsenic acid by either potassium iodide or arsenious acid (Manchot's hypothesis).

Alternative Mechanisms for Reactions of Class II

From what precedes, it is clear that a study of the rates at which inductor and acceptor are acted on by the oxidizing agent (actor) is sufficient to assign each case studied to one of three classes; and in particular, that cases of induction which can be explained on Manchot's hypothesis may be distinguished by this means from those which can not.

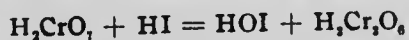
The results of the rate measurements, on the other hand, may often be explained equally well by several different hypothetical mechanisms, within the same group. Mr. De Lury's experiments with chromic acid, arsenic, and potassium iodide, for instance, may be accounted for by assuming either As_2O_3 , Cr_2O_3 , or their hydrates, or some Cr-As compound of a suitable state of oxidation, as the primary product of the action of chromic acid on arsenious acid.

The method of "suitable variation of the reagents" leads to no definite conclusion as to which of these assumptions is the best. True, the reaction between chromic acid and iodides is induced by ferrous salts and by tartaric acid as well as by arsenious acid, which seems to point to the chromic acid as the "specific" and the arsenic as the "unspecific" reagent, and thus to support the Cr_2O_3 hypothesis; the As_2O_3 theory, however, is suggested by the occurrence of numerous reactions in which arsenious acid plays the part of inductor, and although iodides are not mentioned as acceptors in any of the cases recorded in Luther's tables, this may be due to

the difficulty of finding another oxidizing agent which (like chromic acid) acts on arsenic quicker than on potassium iodide.

It is possible, on the other hand, that further rate measurements may lead to the adoption of one of the three theories rather than the others; although, as all three lead to the same conclusions with regard to the induction just studied, this might at first sight seem impossible.

For example, the fact that in dilute solutions the rate of oxidation of potassium iodide by chromic acid¹ is proportional to the concentrations of the iodide and bichromate, may be accounted for by assuming the reaction



in which the hypothetical $\text{H}_2\text{Cr}_2\text{O}_7$ (a hydrate of the Cr_2O_7 of page 18) is taken as "primary product." But if this view of the reaction between chromic and hydriodic acids be combined with the Cr_2O_7 explanation of the induction by arsenious acid, it follows that hydriodic acid must act as inductor to the reaction between arsenious and chromic acids, that the two reactions must be reciprocally inductive in fact; and it is even possible to calculate the effects of the concentrations on the rates and on the induction factor in one case from a knowledge of the other.

As the rates at which chromic acid oxidizes hydriodic and arsenious acids, respectively, are different functions of the concentrations of the acid, it may be possible to increase the former and decrease the latter sufficiently to render these relations accessible to experimental investigation. Such experiments, if carried out, would remove one more degree of freedom from the imagination when inventing "mechanisms" to explain the phenomena of chemical induction.

Summary

The methods hitherto proposed for classifying cases of chemical induction are unsatisfactory.

A new classification is proposed, based on kinetic measure-

¹ Jour. Phys. Chem., 7, 239 (1903).

ments. According to this, the induced reactions are divided into three classes: (i) cases of catalysis combined with destruction of the catalyser, (ii) cases in which the reaction between actor and inductor is the same whether acceptor be present or no, (iii) cases in which it is not.

Only two induced reactions have as yet been studied from this point of view; they furnish typical examples of classes ii and iii.

Reactions of class ii can be explained equally well by several different hypothetical mechanisms (including Manchot's peroxide hypothesis), all of which predict the same kinetic relations. The choice may be narrowed, however, by further kinetic experiments.

*The University of Toronto,
December, 1906*





