3. Lattice parameter measurements of α-cobalt give no evidence of any solid solution of carbon in α-cobalt in a partly carburized sample.

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Sensitized Catalysis. I. The Fundamental Facts

BY HUGO J. KAUFFMANN

The catalytic oxidation of an acid *indigo carmine* solution by hydrogen peroxide shows peculiarities that are not met with other dyes. The indigo carmine is known as a readily oxidizable substance, and just this property is the cause of its exceptional behavior, giving us, as the following investigations demonstrate, new and significant information about catalysis.

Oxidation turns the color from blue to yellow, the latter color not being intense. By using very dilute dye solutions, about 10^{-5} molar, the yellow color is no longer detectable. Such dilute solutions were used for the photometric study of the kinetics. For the qualitative investigations, more concentrated solutions were taken, the duration of the fading, until the last blue or green shade had disappeared, being a measure of the bleaching time. The dye is no longer detectable in concentration of approximately 1×10^{-7} molar. The dye used was water soluble sodium indigo disulfonate, hereafter simply referred to as indigo.

As in the case of other organic compounds, iron salts are the best catalysts and the reaction rate is slower with higher hydrogen ion concentration. The choice of the acid is important; any unnecessary interference in the oxidation process should be avoided. Difficulties are to be expected, if the acid has a high tendency for forming complex iron salts or if the acid is oxidizable. For that reason, the solutions used were generally not buffered and any detrimental change in the *p*H was prevented by application of a large excess of acid. Most investigations were made with solutions of ferric sulfate in sulfuric acid and with ferric perchlorate in perchloric acid. The hydrogen peroxide was present in every case in very large excess.

The Accelerators

The First Facts.—Bubbling illuminating gas through an acid indigo solution containing ferric ion and hydrogen peroxide greatly accelerates the bleaching rate of the dye. The velocity of the gas stream is without appreciable influence on the rate, provided care is taken to maintain a constant temperature. Table I shows the effects with different concentrations of the acid.

TABLE I

10^{-4} mole of indigo, 0.1 mole of H_2O_2 and 10^{-5} g. atom of Fe per liter at 25°.

No.	H_2SO_4, N	Bleaching time, min. in air	Bleaching time, min. in gas
1	0.01	63	35
2	.02	114	52
3	.03	160	68

Washing the gas with permanganate solution did not remove the accelerating substance. Experiments with methane showed a rate acceleration similar to that found for illuminating gas.

The same results occurred when shaking the indigo solution with hydrocarbons, *i. e.*, petroleum ether, heptane, cyclohexane, benzene, toluene, xylene and naphthalene.

The most effective of these substances was benzene which, although only very little soluble in water, showed a bleaching time of four, six and eight minutes, respectively, when substituted for illuminating gas in Table I. For that reason, benzene was chosen for further investigation.

Naphthalene was found to be less effective and very sensitive to the operating temperature. It worked slowly below 25°. Raising the temperature eliminated the acceleration.

Since hydrocarbons are only slightly soluble in water, their sulfonates were prepared and tested. Commercial sulfonates often contain iron and are usable only after careful purification. The normal salt effect; as tested with sodium sulfate, nitrate or perchlorate, was negative. With the sulfonates, on the other hand, the salt effect was strongly positive. Sodium benzene- and *p*-toluenesulfonate were found to be good accelerators, also dipotassium *p,p'*-diphenyldisulfonate.

Magnesium sulfonates, likewise, were suitable and advantageous in those cases where the purification of the magnesium salts was easier and where the ionic strength of the indigo solution was increased by addition of magnesium sulfate or perchlorate. An example is magnesium *p*-dichlorobenzenesulfonate which shows that chlorine compounds can also be accelerators. Inorganic chlorine compounds, such as sodium or magnesium chloride, retard the catalytic indigo oxidation.

The ability of a sulfonate to accelerate depends upon its constitution, being very evident in naphthalene derivatives. The sodium naphthalene-β-sulfonate is only a weak accelerator, whereas the disodium naphthalene-1,5-disulfonate is a powerful one, suited for further experimental studies.

Other Organic Compounds.—Like the hydrocarbons and their sulfonates, many other organic compounds are powerful accelerators. Their efficiency is a matter of constitution, but not bound to a specific structure, because representatives are found in almost all classes of organic substances. Carboxylic acids, alcohols, aldehydes and ketones are suited, especially if they are water soluble. Aliphatic amines are accelerators; aromatic amines, on the contrary, are inhibitors. Phenol and resorcinol are inhibitors. Hydroquinone and catechol act under certain conditions as accelerators, under other conditions as inhibitors, and the study of their fluctuant behavior is one of the ways to clarify the whole problem.

Pyridine does not accelerate; however, quinoline does in high degree, and *o*-phenanthroline is one of the best accelerators.

Tables II and III give a survey of the efficiency of different kinds of substances. Each sample was purified and used only if it was free from iron or so low in iron that this trace could not have any substantial influence. Certain substances defied every attempt of purification and had to be prepared in an unusual way.

TABLE II

9.8 × 10^{-6} mole of indigo, 10^{-2} mole of H_2O_2 and 2×10^{-6} g. atom of Fe in 100 ml. of 0.1 *N* H_2SO_4 at 25°.

Accelerator	Grams in 100 ml. solution	Bleaching time in minutes
None	..	158.2
Methyl alcohol	0.01	30.9
Methyl alcohol	.05	11.2
Methyl alcohol	.10	9.5
Methyl alcohol	.50	9.0
Methyl alcohol	1.00	7.8
Methyl alcohol	2.00	7.6
Ethyl alcohol	1.00	9.4
n-Propyl alcohol	1.00	8.0
i-Propyl alcohol	1.00	32.0
n-Butyl alcohol	1.00	6.2
t-Butyl alcohol	1.00	21.2
Glycerol	1.00	6.3
Sorbitol	1.00	4.5
Ethyl ether	0.71	6.2
Acetone	1.00	4.7
Dextrose	1.00	5.9
Acetic acid	1.00	11.0
Succinic acid	1.00	5.2
Crotonic acid	1.00	4.3
Acetamide	1.00	11.5
Sodium benzenesulfonate	1.00	9.2
Magnesium *p*-toluenesulfonate	1.00	6.5
Disodium naphthalene-1,5-disulfonate	1.00	5.0
Dipotassium diphenyldisulfonate	1.00	19.9

TABLE III

9.8 × 10^{-6} mole of indigo, 10^{-2} mole of H_2O_2 and 2 × 10^{-6} g. atom of Fe in 100 ml. of 0.1 *N* H_2SO_4 at 25°.

Accelerator	Added to to 100 ml. solution	Bleaching time in minutes
None	..	158.2
Benzene	1 ml.	9.6
Benzene	2 ml.	9.6
Cyclohexane	1 ml.	11.4
Benzoic acid	1 g.	12.7
Coumarin	1 g.	8.0
p-Toluenesulfonyl amide	1 g.	4.3

Such a substance was sodium benzenesulfonate, a ground-pillar of the investigation. A product free from iron, from chloride and sulfate ions, from benzenedisulfonates and from diphenylsulfone was obtained by hydrolysis of benzenesulfonyl chloride. The chloride was heated on a water-bath with 5 parts of water until it was completely dissolved after a fortnight. The solution was evaporated in a Vycor dish, the residue treated with water and the separated diphenylsulfone filtered off. The filtrate was neutralized with sodium carbonate to *p*H 7 and after concentrating, mixed in heat with a large quantity of acetone. The precipitate, after washing with acetone, was repeatedly crystallized from water. The acetone treatment removed the last traces of diphenylsulfone which, if pulverized, is a good accelerator.

The figures in the tables are the average of several determinations. The end-point of the reaction was found by comparing the solution with a solution bleached beforehand. The method is not very accurate, but gives values generally reproducible within ±2%.

As the starting point of the reaction, the moment was taken when 10 ml. of a molar hydrogen peroxide solution was mixed with 90 ml. of a solution containing the other constituents. On use of slightly soluble compounds, as in Table III, half of the powdered substance was stirred with the 90 ml. solution and the other half with the 10 ml. of hydrogen peroxide. After fifteen minutes of stirring, both parts were mixed. Without this precaution the bleaching time was longer.

Other Oxidizing Agents.—So far, all facts indicate that the cause of the accelerating power is an inherent property of an organic compound. If this concept is correct, then the hydrogen peroxide is only an aid in revealing this property and must be replaceable by other oxidizing agents. That can really be done.

Peroxydisulfates act similarly to hydrogen peroxide. Substances such as ether, benzene, sulfonates or phenanthroline, are powerful accelerators in this case also.

Periodates are likewise usable. Certain hydroxy compounds, capable of reacting directly with periodic acid without catalyst, are inhibitors for the indigo reaction.

Peroxymonosulfonic acid, generally regarded as a strong oxidizing agent, does not behave in this way with indigo. At low *p*H, even in the presence of an iron salt, it takes a long time until the blue color disappears. Other peracids likewise react slowly with indigo.

In this communication, only research with hydrogen peroxide and with peroxydisulfates is discussed. The action of other oxidizing agents will be described in later papers, as will the influence of diverse metal salts.

Many attempts were made to replace the indigo by another dye, thus far without any success. Instead of an acceleration, retardation took place and the accelerators became inhibitors. An exception was *o*-phenanthroline, the only substance which caused accelerations with methyl orange and methyl red and several other dyes; however, the rate was considerably lower than with indigo. The solutions had to contain much iron and had to be strongly acid. The effect was quite clear with a 5×10^{-3} molar ferric sulfate solution in 0.5 *N* sulfuric acid, even with very little phenanthroline, *i. e.*, 5 mg. per 100 ml.

Nature of the Catalytic Indigo Oxidation

Sensitizer Definition.—Sensitivity to added organic compounds is much higher if copper is the catalyst for the indigo oxidation. The peculiarities of the copper effect shall be described in a later paper and noted here only as far as it is necessary for the comprehension of the iron effect.

A characteristic example is a solution in 0.1 *N* sulfuric acid, containing 10^{-3} mole of copper sulfate, 5×10^{-2} mole of hydrogen peroxide and 2×10^{-5} mole of indigo per liter. Despite the enormous excess of hydrogen peroxide and despite the large amount of catalyst, the solution, kept in the dark at room temperature requires a full week for bleaching.

On shaking with benzene, bleaching is accomplished within one minute. This hydrocarbon, therefore, is capable of intensifying the oxidation rate ten thousand times.

An effect of this kind may be called a *sensitization* and the substance causing it a *sensitizer*. The term sensitizer will be applied only to substances for which the following two conditions are fulfilled: (1) The substance accelerates in the presence of iron as well as in that of copper. (2) The substance does not reduce ferric salts in acid solution. Thus, not every accelerator can be regarded as a sensitizer. A substance which can accelerate without being a sensitizer is hydroquinone. Used in very small quantities at a higher *p*H and at higher iron concentrations, it is a good accelerator, but in most other cases it is a true inhibitor. It readily reduces ferric salts and, therefore, is no sensitizer.

Sensitizers, such as benzene and its sulfonates, do not reduce ferric salt and are very resistant to oxidation; even permanganate and ceric salts hardly attack them.

The above stated conditions refer to periodic acid and percompounds, such as hydrogen peroxide or persulfates. Other oxidizing agents, such as nitric or nitrous acid, work without catalysts and do not give rise to sensitizations.

The Action of Ferric Salts.—Sensitization is connected with the presence not only of the catalyst but also of the percompound. This is evidenced by the behavior of indigo toward iron salts in the absence of a percompound. Ferric salts oxidize indigo, however, without any acceleration by benzene, ether or other sensitizers.

Colorimetric measurements with ferric sulfate as the oxidizing agent show that with large quantities of iron, the rate is at first high, but that the reaction soon slows down and stagnates, although much ferric salt is still present. Two factors are the cause of this stagnation: the hydrogen ion concentration and the formation of ferrous iron.

At lower iron concentrations, comparable with those used in the catalytic oxidations, the reaction proceeded very slowly from the beginning. A solution in 0.01 *N* sulfuric acid, containing 2×10^{-5} mole of indigo and 2×10^{-4} mole of ferric sulfate per liter, showed an indigo decrease of 12% in the first hour, but was still slightly blue after three weeks.

o-Phenanthroline hastens the iron action. Addition of 86 mg. of this substance to one liter of the same solution turns the color slowly violet; after ten minutes, brown; and within an hour, red. Decomposing the ferrous phenanthroline complex by boiling with acid removes the brown color and regenerates the blue. The brown color is probably due to dehydroindigo disulfonate which Wieland[1] assumes to be an intermediate in the indigo oxidation.

Denoting the indigo and the intermediates with the abbreviations Ind, Ind′ and Ind″, the first two steps of the oxidation can be expressed by the equations

$$\text{Ind} + \text{Fe}^{+++} \rightleftarrows \text{Ind}' + \text{Fe}^{++} + \text{H}^{+} \quad (1a)$$

$$\text{Ind}' + \text{Fe}^{+++} \longrightarrow \text{Ind}'' + \text{Fe}^{++} + \text{H}^{+} \quad (1b)$$

Equation (1a) explains the hindrance by H^+ and Fe^{++}. Ind″ means the dehydroindigo disulfonate which is brown and is further oxidized to isatin sulfonate.

These results might promote the theory that the catalytic indigo oxidation rests only upon the oxidation of the indigo by the trivalent iron and the regeneration of the latter by the percompound. The catalysis would appear as a chain reaction in which the iron ion alternates between the bivalent and the trivalent stage.

The Tetravalent Iron.—Such a theory offers no possibility for an explanation of the sensitization. Its shortcomings can be demonstrated by direct experiments. The error is that the bivalent iron ion is regarded as a brake; in reality it is the genuine cause of the high oxidation power of the solution.

Stirring a ferric salt into an acid indigo solution containing a large excess of hydrogen peroxide or of a persulfate, brings about only a slow oxidizing effect. Using a ferrous salt gives a quite different result, an almost instantaneous destruction of the color. The speed of the decolorization depends on the quantity of the ferrous compound; being greater with smaller quantities. The powerful bleaching action is not surprising, because it is

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(1) H. Wieland, *Ber.*, **54**, 2353 (1921).

nothing else but a Fenton[2] reaction applied to a dye.

Most of the tests were made with persulfates at +2°. A liter of 0.1 N sulfuric acid, containing 5 g. ammonium persulfate and 2×10^{-5} mole of indigo, was bleached in nine seconds if 50 mg. of Mohr salt were stirred into the solution and in eleven seconds if 100 mg. were used.

In another experiment at the same temperature, 990 ml. of 0.01 N sulfuric acid, containing 2 g. of potassium persulfate and again 2×10^{-5} mole of indigo, were bleached in eighteen seconds if 0.1 g. of Mohr salt in 10 ml. of water was rapidly stirred into the solution. Ferrous salt was still present after the indigo was bleached and could be detected with ferricyanide for at least eight minutes.

Solutions just having been bleached were still active and oxidized new quantities of indigo very fast. The test with ferricyanide was in every case positive, even in experiments at room temperature. After a certain time, the high activity disappeared but could be regenerated by repeated additions of Mohr salt.

These experiments leave no doubt that the chief oxidizing agent is not the trivalent iron but a substance formed in the reaction of the ferrous ion with the percompound. Taking the simplest formulation, this substance can only be tetravalent iron, for which Bray and Gorin[3] used the formula FeO^{++} of a ferryl ion.

On the assumption that all kinds of percompounds produce the very same tetravalent iron ion, the formula $Fe(OH)^{+++}$ may be suggested. With it the reaction of the ferrous ion with peracids, for example with Caro acid, leads to the simple equation

$$SO_5H^- + Fe^{++} = Fe(OH)^{+++} + SO_4^{=} \qquad (2)$$

The tetravalent iron must be a substance with extremely high oxidation power and capable of oxidizing indigo and dehydroindigo readily. In performing this action it is reduced to bivalent iron. Therefore, the catalysis is a chain reaction in which the iron alternates between the bivalent and tetravalent state.

The oxidation of indigo and dehydroindigo by the tetravalent iron can be represented by

$$\text{Ind} + Fe(OH)^{+++} = \text{Ind}'' + Fe^{++} + H_2O + H^+ \qquad (3a)$$

$$\text{Ind}'' + Fe(OH)^{+++} + H_2O = 2\ \text{Isa} + Fe^{++} + H^+ \qquad (3b)$$

Isa is an abbreviation for isatinsulfonate.

Chain Ruptures.—Bivalent and tetravalent iron are in the solution simultaneously during the catalysis and react with each other either directly or via free hydroxyls. Whatever the way may be, the reaction means a chain rupture slowing down the indigo oxidation. As the function of a sensitizer is just the contrary, the following interpretation arises: benzene and the other sensitizers prevent chain ruptures.

Using this interpretation as working hypothesis, benzene can be regarded as an agent to investigate chain ruptures. An indigo oxidation which can be accelerated by benzene, is a catalysis with chain ruptures. High acceleration would indicate a high number of chain ruptures. The cited example with copper as catalyst would attest that the number of chain ruptures is far higher with copper than with iron.

The chain rupture is expressed by the equation

$$Fe^{++} + Fe(OH)^{+++} \longrightarrow Fe(OH)^{++} + Fe^{+++} \qquad (4)$$

or assuming free hydroxyls by

$$Fe(OH)^{+++} \longrightarrow Fe^{+++} + HO \qquad (5a)$$

$$Fe^{++} + HO \longrightarrow Fe(OH)^{++} \qquad (5b)$$

The Fundamental Equation.—Whether the catalytic indigo oxidation takes hours or seconds, in no case is a brown intermediate detectable. This result is in full agreement with the experiences of others and indicates that the dehydroindigo disulfonate has only a very short existence under the conditions of the catalysis. As fast as it is formed, so fast is it further oxidized.

Since Ind′ and $Fe(OH)^{+++}$ also are present in extremely small concentrations, the following set of equations can be established

$$d(\text{Ind}')/dt = 0 \qquad (6)$$

$$d(\text{Ind}'')/dt = 0 \qquad (7)$$

$$d(Fe(OH)^{+++})/dt = 0 \qquad (8)$$

Making use of them and of (1a), (1b), (2), (3a), (3b) and either (4) or (5a), (5b), the mathematical treatment of the problem in the case of persulfates, leads to the *fundamental equation*

$$\frac{d(Fe^{++})}{dt} = -4\frac{d(\text{Ind})}{dt} - 2\,k(Fe^{++})(S_2O_8^{=}) \qquad (9)$$

All influences of ionic strength, complex formation and hydrolysis are expressed in the values of k which is the constant of the reaction,

$$Fe^{++} + S_2O_8^{=} + H_2O \longrightarrow Fe(OH)^{+++} + 2SO_4^{=} + H^+ \qquad (10)$$

The Kinetics with Persulfates.—Equation (9) throws light on the kinetics of the indigo oxidation by persulfates. Colorimetric measurements of the rate in solutions in which the excess of persulfate is very large, show that the oxidation proceeds in three periods. In the first period, lasting a few minutes under conditions of Table IV, a kind of incubation takes place. In the second and principal period, lasting until about 80% of the indigo has disappeared, the oxidation proceeds as a zero order reaction. In the third period, the reaction slows down and the rate decreases.

The explanation is that in the first period more and more Fe^{++} ions are formed and accumulated, until a stationary state is reached. The Fe^{++} concentration becomes constant in the second period which is, therefore, characterized by

$$d(Fe^{++})/dt = 0 \qquad (11)$$

The fundamental equation (9) is reduced to

$$-2\ d(\text{Ind})/dt = k(Fe^{++})(S_2O_8^{=}) \qquad (12)$$

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[2] H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894); Fenton and Jones, *J. Chem. Soc.*, **77**, 77 (1900).

[3] W. C. Bray and M. H. Gorin, THIS JOURNAL, **54**, 2124 (1932).

that is because $S_2O_8^{=}$ is in a very large excess to an equation of a zero order reaction. Table IV shows the result of several measurements made in this second period, with sulfuric acid and with an initial indigo concentration of 9.8×10^{-6} mole per liter. The rate is given as moles of indigo oxidized per minute.

TABLE IV

RATE OF INDIGO OXIDATION IN SULFURIC ACID WITH 0.500 G. OF $K_2S_2O_8$ PER LITER

(Fe) $\times 10^6$ g. atom per liter	H_2SO_4, N	Rate $\times 10^7$
1	0.005	1.45
2	.010	1.38
3	.015	1.09
10	.050	0.81
20	.100	.72

Benzene effects acceleration in all five solutions, indicating many chain ruptures in each case. These chain ruptures predominate in the third period.

These investigations encountered several experimental difficulties. The principal difficulty was that the concentrations cannot be changed at will. The reactions have to proceed with a certain slowness, otherwise it is impossible to make readings. The rate is sometimes so high that before readings can be started, the color has completely faded.

Another complication is that persulfates cause salt effects and increase the ionic strength. The solution with less persulfate, therefore, has too high a rate. This inconvenience can be overcome in compensating the differences of the ionic strength by the addition of potassium sulfate. However, there is a limit because alkali salts precipitate the dye. Magnesium ions have no salting-out effect and magnesium sulfate is a useful expedient to slow down the rate and to control the ionic strength. The stationary state is less marked in the presence of magnesium sulfate, but the test with benzene reveals that chain ruptures still take place.

The Hydroxyl.—The chain theory of catalytic oxidations by hydrogen peroxide assumes that the chain carrier is the free hydroxyl radical. Application of this theory to the oxidation of indigo leads to the mechanism formulations

$$\mathrm{HO} + \mathrm{Ind} \longrightarrow \mathrm{Ind}' + \mathrm{H_2O} \qquad (13a)$$

$$\mathrm{Ind}' + \mathrm{H_2O_2} \longrightarrow \mathrm{Isa} + \mathrm{Ind}''' \qquad (13b)$$

$$\mathrm{Ind}''' + \mathrm{H_2O_2} \longrightarrow \mathrm{Isa} + \mathrm{HO} + \mathrm{H_2O} \qquad (13c)$$

Ind''' means the last intermediate and can be regarded as the monomer $C_8H_5NSO_5^-$ of isatide disulfonate.

As shown by calculation, the above or similar formulations, if transferred to persulfate, are not capable of explaining the observed zero order reaction and are, therefore, of no help in this problem. This result gave rise to the first doubts as to whether the hydroxyl still is the chain carrier, in cases in which the catalyst is present in large quantities or even in larger ones than the substrate.

With persulfate concentrations higher than 0.1 molar and at a *p*H of 3.7 (glass electrode), the indigo oxidation proceeds very fast, so fast that accurate measurements are hampered. Saturated solutions of potassium persulfate containing as little as 10^{-7} mole of ferric sulfate per liter reveal a significant fact. Such solutions do not react in a zero order reaction and do not show sensitization with benzene. In such solutions the chain carrier might actually be the hydroxyl, but in more strongly acid solutions with higher iron and lower persulfate concentrations, the reaction has quite a different character.

The conditions under which the change of the chain carrier takes place are under investigation. Sensitization is an excellent expedient for this clarification.

Summary

1. Hydrocarbons and many other organic compounds accelerate the catalytic oxidation of an acid indigo solution. The ability to accelerate is a constitutional property of the organic compound.

2. Strong accelerations arise with ferric salts as catalyst and hydrogen peroxide as oxidizing agent. Hydrogen peroxide can be replaced by persulfates and certain other oxidizing agents.

3. Accelerators, working with iron as well as with copper, but being incapable to reduce ferric salts, are called "sensitizers."

4. The catalytic indigo oxidation appears to be a chain reaction. Sensitizers seem to work by preventing chain ruptures.

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[4] Original manuscript received December 20, 1945.