

THE MECHANISM OF INHIBITION IN AUTO- OXIDATION REACTIONS.

BY HANS L. J. BÄCKSTRÖM.

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In a paper published last year,¹ I gave some results obtained in a study of three typical reactions showing negative catalysis, *viz.* three auto-oxidation reactions. I was able to show that in all cases the photochemical reaction is a chain reaction, and that the substances which inhibit the thermal reaction have a similar effect on the photochemical reaction. In agreement with Christiansen's theory of negative catalysis, the results indicated, therefore, that the thermal reaction, also, is a chain reaction, and

¹ Bäckström, *ŷ. Amer. Chem. Soc.*, **49**, 1460 (1927).

that the rôle of the inhibitor, in the thermal as well as in the photochemical oxidation, consists in the breaking of reaction chains.

The results obtained in the auto-oxidation of sodium-sulphite solutions containing different alcohols as inhibitors were particularly striking as they revealed a quantitative agreement between thermal and photochemical reaction. They could be represented by the formulæ:—

$$V_d = \frac{k_1}{kC + k_2}; \quad V_l = k_3 V_d = \frac{k_3 k_1}{kC + k_2},$$

where V_l = light rate, V_d = dark rate, C = concentration of alcohol, and k_1 , k_2 , k_3 and k are constants. The value of k depends on the nature of the alcohol, and is a measure of its relative inhibitory power. The formulæ express the facts that, under a given set of experimental conditions, the ratio between the rates of light and dark reaction remain constant, independent of the nature and concentration of the alcohol present, and that both rates are inversely proportional to a sum of two quantities, one being a constant, k_2 , and the other proportional to the concentration of the inhibitor. The form of the equations and the complete analogy between light and dark reaction which they reveal, indicate that the presence of the alcohols does not in any way affect the number of chains started per unit time, but that they act solely by breaking the reaction chains.

The other reactions studied gave results that were similar, although not quite as simple.

The question then arises: what is the mechanism by which the chains are broken by the inhibitor? This is a problem of considerable interest since this mechanism must obviously be closely connected with the mechanism of chain propagation. In a preliminary discussion of this problem in a more recent paper,³ I reached the conclusion that the mechanism by which the chains are broken is probably an induced reaction between the inhibitor and one of the reactants. In favour of this view I may cite the work of Moureu and Dufraisse³ on the oxidation of acrolein and other organic liquids which shows that the inhibition does not last indefinitely, but that the oxidation sets in sooner or later, indicating that the inhibitor is eventually destroyed. Furthermore, as I pointed out in that paper, this would account for the relationship which seems to exist in the slow combustion of phosphorus between the maximum oxidation pressure and the formation of ozone which accompanies this reaction. It may also be recalled that, apparently, the same applies to the only case of inhibition of a *photochemical* chain reaction that has been closely investigated, namely the inhibition of the hydrogen-chlorine combination by oxygen. This reaction is accompanied by the formation of water and, as first suggested by the Chapmans,⁴ the experimental facts may be interpreted as indicating that it is this induced, or "photosensitized," reaction which causes the chains to be broken.

From this point of view the results of Bigelow⁵ on the inhibitory power of the four butyl alcohols in the oxidation of sulphite solutions are significant. He found that the primary, the secondary, and the iso-butyl alcohols, all acted as inhibitors, but that the tertiary had no effect. Since the first three alcohols can be easily oxidized to aldehydes and ketones, whereas the tertiary can only be oxidized with the simultaneous destruction of the

² Bäckström, *Medd. K. Vet.-Akad. Nobelinst.*, **6**, No. 16 (1927).

³ Moureu and Dufraisse, *Compt. rend.*, **174**, 258 (1922), and subsequent papers.

⁴ D. L. and M. C. C. Chapman, *J. Chem. Soc.*, **123**, 3079 (1923).

⁵ Bigelow, *Z. physik. Chem.*, **26**, 493 (1898).

molecule, there seems to be a direct relation between inhibitory power and oxidizability in this case;⁶ and the logical conclusion seems to be that the alcohols are actually oxidized in the process of breaking the reaction chains. Without postulating any special mechanism of chain propagation, the reaction chain may be described as a series of processes whereby the oxidation of one sulphite ion induces the oxidation of another, and so on. The assumption would be, then, that in the presence of the alcohol this sometimes leads, instead, to an induced oxidation of an alcohol molecule, and that this reaction is incapable of inducing further oxidations or, at least, is less efficient than the corresponding reaction involving a sulphite ion.

To test this idea of a relation between inhibition and induced reactions, a series of investigations have been undertaken at Princeton. The first of these has just been completed, and I shall give a brief account of the results obtained.

For this investigation, which was carried out in collaboration with Mr. Hubert N. Alyea, the oxidation of sulphite solutions in the presence of alcohols was selected, since my previous work had indicated that this represents an unusually simple case of inhibition, and also because this is a relatively simple system from an analytical standpoint, the auto-oxidizable substance being an inorganic salt whereas the inhibitors and their transformation products are organic substances. Isopropyl, sec.-butyl, and benzyl alcohols were tried as inhibitors, and in agreement with the theory it was found that they were oxidized to acetone, methyl-ethyl ketone, and benzaldehyde, respectively. The amounts of these substances that were formed were extremely small—as was to be expected on the theory—but Mr. Alyea succeeded in increasing the sensitivity of existing colour tests about ten times, which rendered quantitative determinations possible.

Let us now see what quantitative results we should expect on the theory, and compare them with those obtained experimentally.

The fact that, as shown by the formulæ, the chain length is inversely proportional to the factor, $kC + k_2$, shows that the chains may be broken in two ways: (i) by the alcohol, its activity in breaking the chains being proportional to its concentration, C , and its relative inhibitory power, k ; or (ii) due to some other cause represented by the constant k_2 . We are at present concerned only with the former of these two processes.

If we make the assumption that the induced oxidation of the inhibitor is completely incapable of inducing further oxidations, *i.e.*, always breaks the reaction chain, then we should expect that every chain which is broken by the alcohol gives rise to the formation of one molecule of the oxidation product, *e.g.*, acetone in the case of isopropyl alcohol. If we call the total number of chains started and broken per minute n , the number of chains broken in that time by the alcohol will be $n \left(\frac{kC}{kC + k_2} \right)$, and this number of acetone molecules will be formed per minute. Since the velocity of sulphite oxidation, V , is expressed by the formula $V = \frac{k_1}{kC + k_2}$, it follows

that the amount of acetone formed in a given time will always be proportional to CV , the product of reaction velocity and inhibitor concentration.

At small inhibitor concentrations this product increases with increasing values of C , and the rate of acetone formation should increase in proportion.

⁶ Compare the theories of Dhar, *Proc. Acad. Amsterdam*, **23**, 1074 (1921); *Z. anorg. Chem.*, **122**, 146 (1922), and Moureu and Dufraisse, *Compt. rend.*, **176**, 624 (1923), linking inhibitory power and oxidizability.

At large inhibitor concentrations, on the other hand, where k_2 is negligibly small compared to kC , this product becomes virtually constant, independent of the alcohol concentration. In this region practically all the chains are broken by the alcohol. Increasing the alcohol concentration causes the chains to be broken sooner, and therefore lowers the rate of sulphite oxidation, but the *number* of chains broken remains the same, and the amount of alcohol oxidized in a given time should therefore remain constant, independent of its concentration.

That this is true is shown by Fig. 1, which represents the data for benzyl alcohol. In the upper graph, CV is plotted against the logarithm of the concentration, the latter being expressed in moles per litre and the reaction velocity in moles per litre per hour. The lower graph gives the amounts of benzaldehyde formed per hour, plotted in the same manner. The full-drawn curve in the upper graph was obtained from the formula

$$V = \frac{0.00029}{C + 0.0012}$$
, the one in the lower graph from the same expression multiplied by a constant factor.

Obviously, it is another consequence of the theory that, within the region

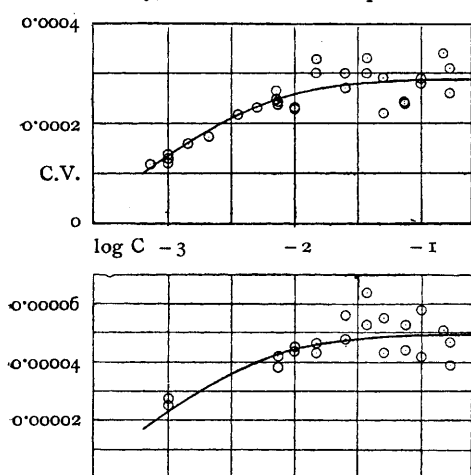


FIG. 1.—Benzaldehyde.

where all the chains are broken by the alcohol, the number of alcohol molecules oxidised in unit time should be the same for different alcohols. The only difference will be that the amounts of these which have to be added in order to reach this region will vary inversely as their specific inhibitory powers, k . This is shown by Table I. which summarises the data for the three alcohols studied. Column 2 gives the range of concentrations within which CV , as well as the rate of the induced oxidation, were found to be constant within

limits of error. Column 3 gives the average CV -values within that range, column 4 the corresponding values of k , and the last column the average amounts of the oxidation products formed, in moles per litre per hour.

TABLE I.

Alcohol.	Concentration Range, Moles/Litre.	$CV \times 10^4$.	Inhibitory Power, k , (from CV).	Oxidation Product Formed.	Rate of Induced Oxidation, Moles/lit./hour.
Isopropyl	0.05 - 1.5	34	3.0	Acetone	0.000046
Sec.-butyl	0.15 - 1.8	103	1	Methyl-ethyl ketone	0.000049
Benzyl	0.0073 - 0.167	2.8	37	Benzaldehyde	0.000048

When two alcohols are present in the solution at the same time, they should be oxidized in proportion to their concentrations and relative

inhibitory powers, but the total number of molecules oxidized in a given time should still be the same. This was verified for an equi-molar mixture of benzyl and isopropyl alcohols. The total number of moles oxidized per litre per hour was 0.000044, the two alcohols sharing in this total in the ratio of 13 : 1. The CV values of Table I. give a ratio of the inhibitory powers of 12 : 1.

The applicability of the theory to the photochemical reaction was tested in a series of experiments with isopropyl alcohol. The light source was a mercury arc which was used with a chlorine-bromine filter. Just as with the thermal reaction, it was found that both CV and the rate of acetone formation were independent of the concentration of the alcohol over the range 0.05 – 1.5 moles per litre. As was to be expected, illumination increased the rates of both reactions in the same proportion: CV from 0.0034 to 0.051, *i.e.*, in a ratio of 1 : 15.0; the rate of acetone formation from 0.000046 to 0.00066 (= 1 : 14.3). This shows that in a solution of a given composition the chain length is the same whether the chains are started thermally or photochemically.

The chain length may, however, also be obtained in a different and altogether independent way, *viz.*, from quantum efficiency measurements on the photochemical reaction. If the absorption of a light quantum by the solution always leads to the starting of a reaction chain, *i.e.*, if none of the light-absorbing molecules are again “deactivated” before they have time to react with oxygen, then we must expect the quantum yield to be a measure of the chain length. The fact that both our present work on the induced oxidation and my previous work on the rate of the photochemical reaction include measurements on benzyl alcohol-inhibited solutions, made under comparable experimental conditions, enables us to decide this point. My previous measurements, that were made in monochromatic light of wavelength $254\mu\mu$ and of known absolute intensity, could be represented by a formula which, when applied to a solution containing 0.1 mole of benzyl alcohol per litre, gives a quantum yield of 64 molecules per $h\nu$. On the other hand, the data in Table I. show that the chain length at this alcohol concentration, which is well within the region where all the chains are broken by the inhibitor, is equal to $28/0.48 = 58$ molecules. This is an agreement which can hardly be accidental.

As regards the photochemical reaction, we may express this result by saying that the induced, or “photosensitized,” oxidation of the alcohol obeys the Einstein photochemical equivalence law. Exactly the same result was obtained by Cremer⁷ in a study of a reaction to which I have referred earlier in this paper, *viz.* the photosensitized formation of water which accompanies the hydrogen-chlorine combination when oxygen is present.

Finally, we have also made some measurements on the copper-catalysed reaction which show that copper salts accelerate the total reaction without changing the ratio of sulphite oxidized to alcohol oxidized, *i.e.* without altering the chain length.

Summarizing the results of this investigation, it may be said that they seem to furnish a new and rather direct proof of the existence of thermal chain reactions; and that they throw some light on the mechanism by which reaction chains may be broken by an inhibitor.

Princeton University,
Princeton, N.J., U.S.A.

⁷ Cremer, *Z. physik. Chem.*, **128**, 285 (1927).