567. *The Kinetics of the Rearrangement and Oxidation of Hydrazobenzene in Solution. Part II.* The Catalysed Oxidation.*

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The ions of many metals catalyse the oxidation of hydrazobenzene in alkaline solutions containing oxygen, but cupric ions are outstandingly effective. The catalyst cycle involves the rate-determining acceptance of one electron by cupric ions from a substrate consisting of singly charged ions produced by the first (acid) dissociation of hydrazobenzene. The rate of the reaction is independent of the oxygen concentration once a certain critical value is exceeded. A similar limit is reached on increasing the concentration of the catalyst. The latter behaviour, coupled with the dependence of rate on pH, leads to the conclusion that the catalyst is a colloidal solution of cupric hydroxide, which enters into an oxidation-reduction cycle.

IN the preceding paper it was noted that the oxidation of hydrazobenzene by oxygen in alkaline solution is catalysed by trace amounts of metal ions. The present paper is concerned with the mechanism of this catalysed oxidation.

EXPERIMENTAL

Materials and techniques were as in Part I. Solutions containing very small quantities of metal ions were prepared by systematic dilution. Blackened reaction vessels were used and for certain experiments under oxygen-free conditions the apparatus used was that devised for the measurement of the rate of rearrangement of hydrazobenzene. In other cases the reaction mixtures were saturated with air or a mixture of oxygen and nitrogen as already described.

RESULTS

The reaction was of the first order with respect to variation in the initial concentration of hydrazobenzene but as rate constants tended to fall off with time initial rates were used to calculate a pseudo-first-order rate constant, *k*, for each run. A preliminary survey was carried out in order to determine which catalysts were most suitable for further study. Reaction mixtures 10^{-5} molar with respect to a metal-ion catalyst were used and the hydrazobenzene concentration was 10^{-3} mole/l. Cupric ions proved to be about nine times more effective than the ions of any other metal under the experimental conditions (see Table 1).

TABLE 1. *Relative effect of different metal ions on the rate of oxidation at 25° in solutions of* pH 13 *saturated with air.*

	% change in *k*
Copper	750
Chromium, cobalt, uranium	50—90
Nickel, titanium, manganese, silver, gold, iron	10—40
Lithium, sodium, potassium, rubidium, cæsium, calcium, strontium, barium, beryllium, magnesium, cadmium, zinc, thallium, mercury, lead, boron, tungsten	0

The catalytic effect of cupric ions was studied under different conditions. In presence of 10^{-5} mole of cupric chloride per litre at pH 10 the rate of reaction becomes independent of the oxygen concentration once a small value has been exceeded. The dependence of the rate on catalyst concentration was studied at pH 10 and at pH 13 in mixtures saturated with air (Figure). The nature of the catalytic cycle was next established as follows. When oxygen is excluded from reaction mixtures containing relatively large quantities of cupric chloride azobenzene is produced, indicating that cupric ions alone are capable of carrying through the complete oxidation process. There is, of course, no regeneration of the catalyst in absence of oxygen and the reaction very soon comes to a stop. The stoicheiometry of the process was found to be as shown, cupric ions being reduced to the cuprous stage and no further :

$$\mathrm{PhNH{\cdot}NHPh + 2Cu^{++} \longrightarrow PhN{:}NPh + 2H^{+} + 2Cu^{+}}$$

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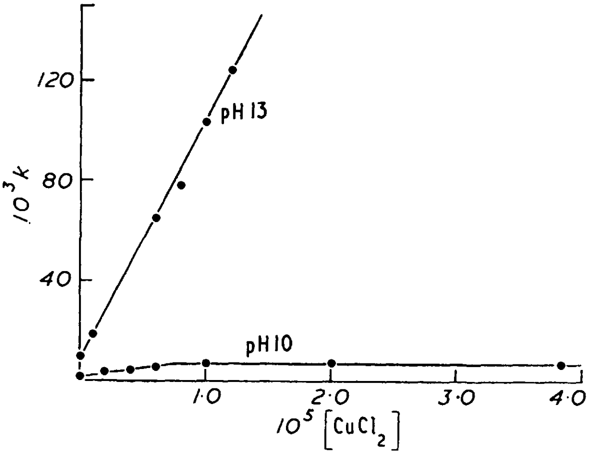
* Part I, preceding paper.

This was proved by preparing reaction mixtures containing different amounts of cupric chloride but no oxygen. After a suitable time excess of edta was added, with exclusion of oxygen, in order to bind the copper and so reduce its catalytic activity. This made it possible to estimate the amount of azobenzene produced under the oxygen-free conditions without any serious error due to the usual catalysed oxidation which would taken place when samples were exposed to the atmosphere. The results are in Table 2. The first row represents the expected oxidation in terms of the equation given above.

TABLE 2. *Oxidation by cupric ions.*

Expected (%)	25	37·5	50	72·5
Observed (%)	31	47	55	76
Cupric chloride (moles/litre × 10^3)	0·50	0·75	1·00	1·45

It was noted that although the catalytic effect of cupric ions is markedly reduced when they are bound by edta this compound itself shows some catalytic activity, an interesting effect which merits further study. The catalysis is not due to contamination of the edta with metal ions, as an ignition test, similar to that applied to hydrazobenzene, showed it to be ion-free.



The solubility product of cupric hydroxide was exceeded throughout the determinations of reactions rates by a factor of at least 10^6 yet no precipitation occurred. This suggested that the catalyst was present in the form of a colloid, stable at least for the period of an experiment. Reaction mixtures containing the same amount of cupric chloride were subjected to high-speed centrifugation for varying lengths of time immediately before the runs. A complex, pH dependent, change in the rate was observed supporting the idea of catalysis by a rather sensitive colloidal system. At pH 10 the rate of the reaction (k, sec.$^{-1}$) becomes independent of the cupric chloride concentration (moles l.$^{-1}$) (Figure) once a small critical concentration has been exceeded, but no such limit is detectable at pH 13. A limit is observed for catalysis by silver or gold at pH 13. These effects are difficult to explain except in terms of the colloidal nature of the catalysts.

DISCUSSION

The form of the catalyst cycle is clear from the experimental evidence. Cupric ions accept one electron, are reduced to the cuprous state and are rapidly re-oxidised by oxygen. The rate-determining step of the spontaneous oxidation has been assumed to be the second ionisation but in the very much faster catalysed reaction this can no longer be true. The cupric ions probably accept an electron from the first ion and the reaction sequence may be set out as follows:

$$(1)\quad \mathrm{PhNH{\cdot}NHPh} \rightleftharpoons \mathrm{PhN^{-}{\cdot}NHPh} + \mathrm{H^{+}} \quad . \quad . \quad K_1 = k_1/k_{-1}$$

$$(2)\quad \mathrm{PhN^{-}{\cdot}NHPh} + \mathrm{Cu^{++}} \longrightarrow \mathrm{Cu^{+}} + \mathrm{PhN{\cdot}NHPh} \quad . \quad . \quad . \quad . \quad k_2$$

$$(3)\quad \mathrm{PhN{\cdot}NHPh} + \mathrm{Cu^{++}} \longrightarrow \mathrm{Cu^{+}} + \mathrm{H^{+}} + \mathrm{PhN{:}NPh} \quad . \quad . \quad . \quad k_3$$

$$(4)\quad \mathrm{Cu^{+}} + \mathrm{O_2} \longrightarrow \mathrm{Cu^{++}} + \mathrm{O_2^{-}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad k_4$$

Step (3) is taken to follow very rapidly on step (2) which is rate-determining, and the concentration of cupric ions is assumed to reach a stationary value:

$$(5)\quad d[Cu^{++}]/dt = k_4[Cu^+][O_2] - 2k_2[PhN^-{\cdot}NHPh][Cu^{++}] = 0$$

If [Cu] = total copper = $[Cu^+] + [Cu^{++}]$ and $[Cu^+]$ is replaced by

$$2k_2[PhN^-{\cdot}NHPh][Cu^{++}]/\{k_4[O_2]\}$$

from eqn. (5) then an expression for $[Cu^{++}]$ is obtained by transposition:

$$[Cu^{++}] = \frac{k_4[O_2][Cu]}{2k_2[PhN^-{\cdot}NHPh] + k_4[O_2]}$$

Since

$$[PhN^-{\cdot}NHPh] = K_1[PhNH{\cdot}NHPh]/[H^+]$$

$$-d[PhNH{\cdot}NHPh]/dt = k_2[PhN^-{\cdot}NHPh][Cu^{++}]$$

$$(6)\quad = \frac{k_2k_4K_1[PhNH{\cdot}NHPh][O_2][Cu]/[H^+]}{k_4[O_2] + 2k_2K_1[PhNH{\cdot}NHPh]/[H^+]}$$

This equation has two limiting cases which describe the observed kinetics of the oxidation process:

$$\text{(i)}\quad k_4[O_2] \ll 2k_2K_1[PhNH{\cdot}NHPh]/[H^+]$$

$$(7)\quad -d[PhNH{\cdot}NHPh]/dt = \tfrac{1}{2}k_4[Cu][O_2]$$

$$\text{(ii)}\quad k_4[O_2] \gg 2k_2K_1[PhNH{\cdot}NHPh]/[H^+]$$

$$(8)\quad -d[PhNH{\cdot}NHPh]/dt = k_2K_1[PhNH{\cdot}NHPh][Cu]/[H^+]$$

The above treatment takes no account of the fact that at pH dependent, critical concentrations of the catalyst the rate becomes independent of the catalyst. This effect is best discussed separately since it is a function of the catalyst rather than of the catalysed reaction. At pH 10 the critical concentration of cupric chloride is less than 10^{-5} mole/l. for solutions saturated with air but contrary to what might have been expected the rate of the reaction in presence of 10^{-5} mole/l. is not increased by saturating the solution with pure oxygen. Moreover, the concentrations at which the rate ceases to increase are different for silver and gold which show critical values in media at pH 13 where no limit is detectable with copper. These various facts suggest that the explanation must be sought in terms of colloidal phenomena.

The catalyst is probably a colloidal solution of the hydroxide peptised by hydroxyl ions, the solutions being alkaline. The higher the pH the greater the degree of peptisation and the greater the number of micelles for a given concentration of the catalyst. Once the catalyst concentration exceeds a certain value the number of micelles may become effectively constant, further increases in the amount of catalyst present simply increasing the average size of the micelles or leading to coagulation of the small active particles. Ions of the catalyst buried in the core of large micelles are presumably not catalytically available. The pH dependence of the critical concentration can thus be understood.

Equations (7) and (8) both involve a kinetic constant (k_4 or k_2) describing an electron-transfer process associated with the catalyst, the best catalysts for the oxidation of hydrazobenzene in alkaline solution being those susceptible to ready interconversion from one oxidation state to another, in other words those with oxidation states of comparable stability in the colloid micelles.

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