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Mutual Catalysis in the Chromium(III)–EDTA–Hydrogen Peroxide System

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Hydrogen peroxide catalyzes the reaction between hexaaquachromium(III) and ethylenediaminetetraacetic acid, while chromium(III)–EDTA complex accelerates the decomposition of hydrogen peroxide. A mechanism is suggested for the reaction on the basis of gasvolumetric and spectrophotometric experiments.

Yamamoto and Ohashi[1] reported that hydrogen peroxide accelerates the reaction between hexaaquachromium(III) and ethylenediaminetetraacetate in acidic medium. The effect was found proportional to the concentration of hydrogen peroxide. According to the mechanism suggested by the authors hydrogen peroxide oxidizes chromium(III) to chromium(IV) and/or chromium(V) which then reacts rapidly with EDTA. The chromium complex in higher oxidation state can react either with chromium(III) or with hydrogen peroxide:

$$\mathrm{Cr(IV)\text{-}EDTA}\begin{cases}\xrightarrow{\mathrm{Cr(III)}} \mathrm{Cr(III)\text{-}EDTA} + \mathrm{Cr(IV)} \\ \xrightarrow[\mathrm{H_2O_2}]{} \mathrm{Cr(III)\text{-}EDTA} + 1/4\,\mathrm{O_2}\end{cases} \qquad (1)$$

Analogous reactions are also assumed for the Cr(V)–EDTA complex.

However, the reactions with hydrogen peroxide were eliminated from the mechanism since no evolution of oxygen was observed for one half time. Since these reactions seem to be essential we have carried out measurements on the evolution of oxygen.

Experimental

The experimental conditions were the same as those reported by Yamamoto and Ohashi.[1]

Chromium(III) perchlorate was prepared in solution by the reduction of CrO_3 with hydrogen peroxide in perchloric acid medium.

For the experiments 0.1 M EDTA solution and 30% hydrogen peroxide solution were used. The pH was adjusted by use of 0.5 M acetate buffer. The volume of the reaction mixture was 10 ml in each case. Formation of the complex was followed by measring the absorbance of the thermostated reaction mixture (25 °C) at 545 nm using a Beckman Acta III spectrophotometer. From the measured absorbance the concentration was calculated by means of 210 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ molar absorbance of the chromium(III)–EDTA complex.

The evolution of oxygen was followed gas-volumetrically. The hydrogen peroxide solution was first stirred for about 30 min to eliminate the over-saturation of solution by oxygen. Before each experiment the rate of self-decomposition of hydrogen peroxide was checked. The reaction was started when the rate became constant and—within the experimental error—equal to 0.19 ml $\mathrm{min^{-1}}$. The rate of self-decomposition was considered in calculating the rate of the catalyzed reaction of hydrogen peroxide.

Results and Discussion

The decomposition of hydrogen peroxide is enhanced by hexaaquachromium(III) ions as shown in Fig. 1. The shape of the curve suggests that Cr(IV) and/or Cr(V) formed from Cr(III) are the catalysts of the decomposition of hydrogen peroxide in acidic medium. So far no information seemes to have been given on the effect of Cr(III).[2] Spitalsky[3] found that in the reaction between hydrogen peroxide and chromium(VI) the final ratio of Cr(VI): Cr(III) is determined by the initial concentration of hydrogen peroxide. He found that a considerable portion of chromium(VI) can be substituted by Cr(III) without substantial change in the catalytic effect. However, the effect of chromium(III) was not studied exclusively.

The rate of the evolution of oxygen decreases a great deal in the presence of EDTA, indicating that the EDTA complexes are less active catalysts of the decomposition than the corresponding aqua complexes. The difference in the shape of the curves in Fig. 2 shows that catalytically active EDTA complexes of the chromium are of higher oxidation state. The formation of the complex $CrEDTA(H_2O)^-$ is described by a saturation curve, the evolution of oxygen after an acceleration period becoming constant. In contrast to the result of Yamamoto and Ohashi the evolution of oxygen is considerable from the beginning of the reaction.[1]

We have also studied the effect of EDTA in the system chromium(VI)–hydrogen peroxide. Only semi-quantitative data could be obtained because of the lively evolution of oxygen. It is certain that in the presence of an excess of EDTA the total amount of chromium is present as chromium(III)–EDTA complex.

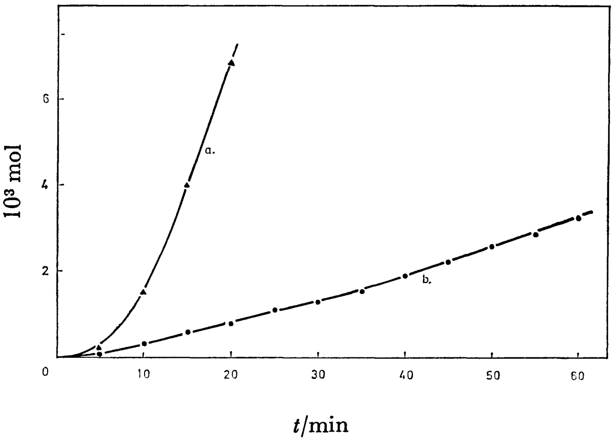


Fig. 1. Kinetic curves of evolution of oxygen in the $Cr(III)\text{-}H_2O_2$ system in the absence (a) and in the presence (b) of EDTA.
$[H_2O_2]=5.0$ M, $[Cr(III)]=7.35\times10^{-3}$ M, $[CH_3COO^-]=0.1$ M, $[EDTA]=2\times10^{-2}$ M, pH$=3.8$, $T=25.0\pm0.1$ °C, 10 ml.

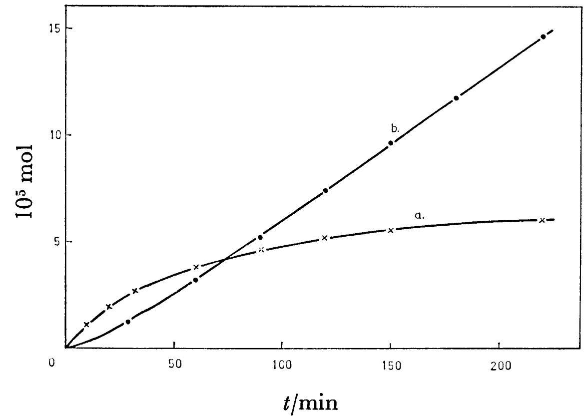


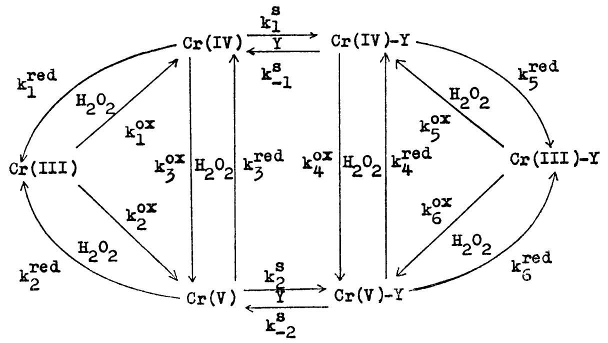
Fig. 2. Comparison of the kinetic curves of complex formation of Cr(III)-EDTA (a) and of evolution of oxygen (b) in the Cr(III)-EDTA-H$_2$O$_2$ system. Conditions are given in the legend of the Fig. 1.

When no EDTA is present, there is an equilibrium between Cr(VI) and Cr(III). The fast initial evolution of oxygen diminishes and the value observed in the system chromium(III)–EDTA–hydrogen peroxide is attained. The formation of Cr(III)–EDTA complex takes place faster when chromium is initially present as chromate.

The reaction mechanism is extremely complicated. The following types of reactions should be taken into account:

1. Redox reactions between hydrogen peroxide and aquo ions of chromium in different oxidation states.
2. Disproportionation reaction of Cr(IV) and Cr(V).
3. Redox reactions between chromium ions in different oxidation states.
4. Substitution reactions with EDTA.
5. Redox reactions betweeen hydrogen peroxide and EDTA complexes of chromium in different oxidation states.
6. Other redox and disproportionation reactions involving EDTA complexes of chromium in different oxidation states.

Starting with Cr(III) in the presence of EDTA we can disregard reactions leading to Cr(VI). In the following scheme only those redox reactions which involve hydrogen peroxide are taken into consideration, visg., reactions of type 2, 3, and 6 are also disregarded. Thus the following scheme can be written:



Y: EDTA. (2)

The network of reactions can be greatly simplified if we bear in mind the data referring to the rate of the formation of the Cr(III)–EDTA complex and that of the evolution of oxygen:

1. According to the rate equation given by Yamamoto and Ohashi[1] the rate determining step is the reaction between Cr(H$_2$O)$_6^{3+}$ and H$_2$O$_2$, k_1^{ox} and k_2^{ox} being the smallest among the rate constants.
2. In order to explain the diminishing effect of EDTA on the rate of the oxygen evolution, we should assume that the equilibrium between Cr(IV) and Cr(V) and EDTA is shifted to the formation of the complex, viz., $k_1^s \gg k_{-1}^s$ and $k_2^s \gg k_{-2}^s$.
3. According to the spectrophotometric measurements (Fig. 2. curve a) the amount of Cr(III)–EDTA complex increases steadily: $k_5^{ox} < k_5^{red}$ and $k_6^{ox} < k_6^{red}$.
4. Since the experimental data do not permit separation of paths involving Cr(IV) and Cr(V), only reactions of Cr(IV) should be considered. This makes the handling of rate equations easier.

The following simple scheme can be written:

$$\mathrm{Cr(III)} \xrightarrow[\mathrm{H_2O_2}]{k_1^{ox}} \mathrm{Cr(IV)} \xrightarrow[\mathrm{EDTA}]{k_1^{s}}$$

$$\mathrm{Cr(IV)\text{-}EDTA} \underset{\underset{\mathrm{H_2O_2}}{k_5^{ox}}}{\overset{\overset{\mathrm{H_2O_2},\ -1/4\,O_2}{k_5^{red}}}{\rightleftarrows}} \mathrm{Cr(III)\text{-}EDTA}$$

$$k_1^s > k_5^{red} > k_1^{ox} \approx k_5^{ox}. \tag{3}$$

The condition of the steady evolution of oxygen is as follows:

$$\frac{d[O_2]}{dt} = \text{constant} = k_5^{red}[\mathrm{Cr(IV)\text{-}EDTA}]. \tag{4}$$

This requires that

$$\frac{d[\mathrm{Cr(IV)\text{-}EDTA}]}{dt} = 0 = k_1^{ox}[\mathrm{Cr(III)}] - k_5^{red}[\mathrm{Cr(IV)\text{-}EDTA}] + k_5^{ox}[\mathrm{Cr(III)\text{-}EDTA}]. \tag{5}$$

Since the concentration of the intermediates is so small that they cannot be detected spectrophotometrically and their existence is indicated only by the shape of the rate curves of oxygen evolution, we have

$$[\mathrm{Cr(III)}] + [\mathrm{Cr(III)\text{-}EDTA}] \approx [\mathrm{Cr(III)}]_0. \tag{6}$$

Thus Eq. 5 can be written as follows.

$$k_5^{red}[\mathrm{Cr(IV)\text{-}EDTA}] = k_5^{ox}[\mathrm{Cr(III)}]_0 - [\mathrm{Cr(III)}](k_5^{ox} - k_1^{ox}). \tag{7}$$

Considering Eqs 4 and 7, we get

$$k_5^{ox}[\mathrm{Cr(III)}]_0 - [\mathrm{Cr(III)}](k_5^{ox} - k_1^{ox}) = \text{constant}. \tag{8}$$

It follows that the steady evolution of oxygen follows from the simplified scheme, if

1. $k_5^{ox} \approx k_1^{ox}$ and/or
2. $[\mathrm{Cr(III)}] \ll [\mathrm{Cr(III)}]_0$.

In the first stage of the reaction, before the formation of the Cr(III)–EDTA complex is completed, only the first condition is fulfilled, while in the later stage of the reactions both conditions can be satisfied. The fact that the rate of the oxygen evolution becomes constant before the complete transformation of Cr(III) to Cr(III)–EDTA indicates that the first condition is actually satisfied:

$$k_5^{\mathrm{ox}}[\mathrm{Cr(III)}]_0 \gg [\mathrm{Cr(III)}](k_5^{\mathrm{ox}} - k_1^{\mathrm{ox}}), \tag{9}$$

causing Eq. 8 to be fulfilled.

The results show that mutual catalysis takes place in the Cr(III)–EDTA–H_2O_2 system. Hydrogen peroxide accelerates the formation of Cr(III)–EDTA, which in turn catalyzes the decomposition of H_2O_2.

References

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