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Catalytic Activity and Complexation. III. Kinetics of the Oxine Activation of a Catalytic Reaction of Vanadium(V)

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The activating effect of 8-hydroxyquinoline (oxine) on the vanadium(V) catalysed oxidation of p-phenetidine with chlorate is further investigated. The rate constant of the oxidation process which takes place in the charge transfer complex (CTC) between the catalyst, the substrate and the activator was determined; the order of the rate constant of the CTC formation was evaluated. It is shown, that the presence of oxine accelerates the CTC formation in a such extent, that rate determining stage of the catalytic reaction becomes the regeneration of the catalyst by the chlorate oxidation of V^{IV} to V^{V}. In this case the over all reaction rate can be further increased using bromate as an oxidant in the process.

Introduction

The action of 8-hydroxyquinoline (oxine) as an activator of some homogeneous catalytic reactions in solution has recently been investigated on the model of the vanadium(V) catalysed oxidation of p-phenetidine hydrochloride by chlorate.[1] It was established that oxine accelerates the initial period of the catalytic reaction, facilitating the complex formation between the catalyst and the organic substrate. In the present work we proceed further the investigations on the mechanism of oxine activation, studying the next stages of the catalytic process and its kinetics as a whole.

Experimental Section

The reaction kinetics was followed photometrically as intensively coloured substances are formed during the course of the reaction.[1] The reagents placed in a glass vessel with three sections[2] were heated in a thermostat for 15 minutes and then mixed by vigorous shaking. The solution was placed in the cell of the photometer (FEK-M) equipped with a device for constant temperature regulation. The absorbancy of the solution was followed as a function of the time, using green filter with $\lambda_{max} = 530$ mμ. The cell length in all cases was 50 mm.

The acidity of the reaction medium was kept constant with buffer solutions, containing phosphoric, boric, acetic acids and sodium hydroxide.

All reagent and buffer solutions were prepared from reagent grade substances and water, twice distilled in Jenaer glass vessel.

Results and Discussion

It was yet established that the catalytic oxidation of p-phenetidine hydrochloride (PHEN) by chlorate and vanadium(V) as a catalst proceeds in many stages.[2] At first a charge transfer complex (CTC) between vanadium(V) and PHEN is formed, in which then a complete transfer of an electron from PHEN to V^{V} takes place. Vanadium(V) is reduced to vanadium(IV) as a result and PHEN is oxidized to imino radicals, which after recombination and hydrolysis of the intermediate give N-(4-ethoxyphenyl)-quinonimine as a final product. The role of chlorate is to oxidize vanadium(IV) to vanadium(V) and thus to regenerate the catalyst. A new reaction cycle then begins again by interaction of V^{V} with PHEN.

Oxine affects the reaction rate taking part in the CTC formation. Because of its strong π-*trans* effect oxine facilitates the entrance of PHEN into the coordination sphere of the catalyst and thus the formation of CTC. It is supposed from the experimental data[1] that the formation of the charge transfer complex [ox-V^{V}-PHEN] proceeds in the following setps: *

$$V^{V} + ox \rightleftarrows [ox\text{-}V^{V}] \quad (1)$$

$$[ox\text{-}V^{V}] + PHEN \rightleftarrows [ox\text{-}V^{V}, PHEN] \quad (2)$$

$$[ox\text{-}V^{V}, PHEN] \rightleftarrows [ox\text{-}V^{V}\text{-}PHEN] \quad (3)$$

In order to simplify the investigation of the system the influence of oxine was studied at first in the absence of chlorate, i.e. on one reaction cycle only. The absorbancy of the reaction solution was followed as a function of the time, the results being present on Figure 1.

In the reaction conditions used above (Figure 1), when the concentration of V^{V} is very small compared to PHEN and oxine concentrations, the formation of CTC proceeds very fast. The stages of the CTC formation (equations (1)-(3)) could not be observed

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(1) P. R. Bontchev and B. G. Jeliazkowa, *Inorg. Chim. Acta, 1*, 249 (1967).

(2) P. R. Bontchev and B. G. Jeliazkowa, *Mikrochim. Acta*, Wien, 125 (1967).

(*) In the equations (1)-(3) vanadium(V), oxine and PHEN are indicated not taking into consideration the forms in which they exist in the solution. This question is discussed in detail in the preceding paper.[1]

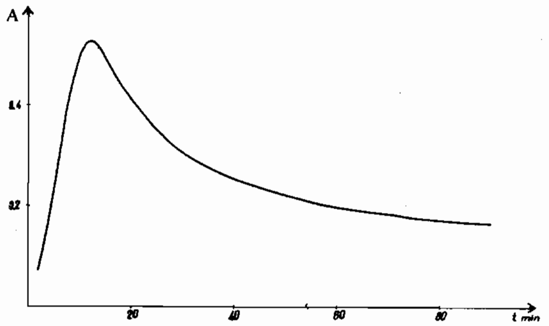

Figure 1. Dependence of the Absorbance of the Reaction Solution on the Time in the Absence of Chlorate. NH_4VO_3, 3×10^{-5}*M;* PHEN, 1×10^{-3}*M;* oxine, $1{,}5\times10^{-3}$*M;* pH 2,0; t° 17,0°C.

by the kinetic data and the formation of CTC can be considered as one total process. Hence, the change of the absorbancy with the time reflects the kinetics of the two main processes — the formation and the consumption of the CTC.[1] The maximum of the curve on Figure 1 corresponds to the maximum concentration of the complex in the system. At the end of the reaction cycle when the concentration of the complex is very low, the curve on Figure 1 shows $A > 0$ because N-(4-ethoxyphenyl)-quinonimine has an appreciable absorbancy in the spectral range used.[1]

The influence of the activator concentration on the kinetics of the reaction was studied in the absence of chlorate. The absorbancy of the reaction system was followed with the time. The results showed that the time, necessary for the development of the maximum absorbancy (A_{max}), depends on the oxine concentration, but the value of A_{max} is approximately the same in all experiments within the limits of ±4%. The fact that the maximum CTC concentration is one and the same despite the different rate of CTC formation indicates that in the initial reaction period (before A_{max}) the rate of the complex consumption is negligibly low in comparison with the rate of its formation. This conclusion is confirmed by the absorption spectra of the system followed with the time. They show that before t_{max} there is no measurable amounts of the reaction product N-(4-ethoxyphenyl)-quinonimine. In other words in a first approximation we could consider that the formation and the consumption of CTC proceed in two stages, practically separated in time. That fact permits to investigate their kinetics using the parts of the kinetic curve before A_{max} and after it.

The time t_{max} necessary for the development of the maximum absorbancy (A_{max}) was used as a measure of the rate of the CTC formation. The dependence of t_{max} on the concentration of the activator is shown on Figure 2. The plot in Figure 2 crosses the origin because at such low concentrations of vanadium(V) there is no detectable CTC formation in the absence of oxine in the pH range used.

It can be seen from Figure 2 that the rate of CTC formation depends linearly on the oxine concentration even at a hundredfold oxine excess with respect to V^V. These data, compared with equations (1)-(3) for the mechanism of activation show that the change in oxine concentration shifts the equilibrium (1) towards the undissociated complex $[V^V\text{-ox}]$.* However these data could not be used for the calculation of the overall rate constant k_f of the CTC formation because the equilibrium constant K_1 (the stability constant of 1 : 1 V^V: oxine complex) is still unknown. It can be suggested only that k_f is several times higher than the rate constant of the CTC consumption k_c.

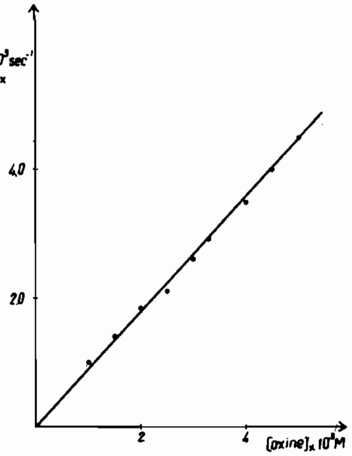

Figure 2. Dependence of t_{max} on the Oxine Concentration. NH_4VO_3, 3×10^{-5}*M;* PHEN, 1×10^{-3}*M;* pH 2,0; t° 17,0°C.

The rate constant k_c of the CTC consumption can be evaluated from the data on Figure 1. The oxidation taking place in the complex is a monomolecular reaction[1] and hence the following equation is valid for the CTC concentration:

$$C = C_o . e^{-k_c . t} \tag{4}$$

where: C is the current concentration of the complex, measured photometrically; C_o is the initial complex concentration (for this value the maximum concentration of CTC is taken, corresponding to A_{max}); k_c is the rate constant of the complex consumption.

For the initial period of this reaction, when $k_c . t$ is a small quantity, the equation (4) can be simplified to

$$\frac{C}{C_o} = 1 - k_c . t \tag{5}$$

Equation (5) combined with Bouguer-Lambert-Beer law gives for k_c the expression

$$k_c = \frac{1}{t}(1 - \frac{A}{A_{max}}) \tag{6}$$

The equation (6) was solved with the data of the kinetic curve on Figure 1. In a first approximation the moment t_{max} was taken as a start point of the process. A_{max} and the corresponding values of A at the moment t were taken in the period of time between the 4th and the 12th minute from t_{max}. The rate constant k_c was determined for eight points in this period and its value was found to be $(4.6\pm0.1)\times10^{-4}$ sec^{-1}.

(*) This conclusion is in a good agreement with the suggested high rate for the establishment of equilibrium (1)[1] as well as with the known data for the formation rate of other oxine complexes.[3]

(3) D. N. Hague and M. Eigen, *Trans. Faraday Soc.*, *62*, 1236 (1966).

The results obtained for the period of time before the 4th and after the 12th minute are somewhat different and time dependent. For the initial reaction period the deviations are due to the approximation that the reaction start corresponds to the moment t_{max}. For values of t, very near to t_{max} this approximation represent an oversimplification. For that reason we did not use the period of time between t_{max} and the 4th minute after it. The deviations of k_c after the 12th minute of the reaction are due to the fact that appreciable amounts of N-(4-ethoxyphenyl)-quinonimine are formed, which affect the course of the curve A/t. If corrections are made in this period of time for the amounts of the reaction product (its extinction coefficient is yet known[1]) the values found for k_c agree well with its value shown above.

The upper investigations refer to the reaction carried out in the absence of chlorate, i.e. only to a sole reaction cycle. They permit the determination of k_c and the order of magnitude of k_f as well ($k_f \sim n \times 10^{-3} sec^{-1}$).

On Figure 3 the kinetics of the catalytic reaction is shown. The reaction is carried out in the presence of oxine and chlorate as well. It follows from Figure 3 that the oxidation of vanadium(IV)

$$V^{IV} + ClO_3^- \rightarrow V^V + Cl^- \qquad (7)$$

is very slow, compared to the formation of CTC and its consumption. For that reason after the first reaction cycle the overall reaction rate is determined by the rate of the slowest stage — the oxidation of vanadium(IV). When the catalytic reaction is carried out in the presence of higher chlorate concentration the rate of the process (7) increases and the course of the kinetic curve is changed (Figure 4 a, b). Analogous results are found if the reaction is carried out at higher temperatures when the process (7) is also preferably accelerated (Figure 4 c, d).

The slowest stage of the catalytic reaction, carried out in the absence of oxine is the formation of CTC from V^V and PHEN. It follows from the upper data that oxine accelerates that stage in such a high extent that the process (7) became the rate determining possible if the oxidation of V^{IV} is carried out with a much higher rate. We tried to receive such an effect increasing the chlorate concentration up to $2.7 \times 10^{-1} M$ and the temperature — up to 60°C as well. Despite the fact that the reaction rate was thus increased in a conciderable extent, the process (7) still remained the slowest, rate determining step of the catalytic reaction. For that reason we try to use another oxidant oxidising V^{IV} with a higher rate. For that purpose sodium bromate was used as an oxidant during the course of the catalytic reaction, the results being shown in Figure 5.

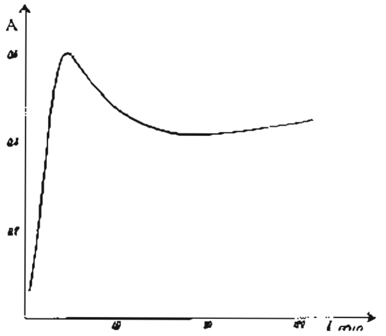

Figure 3. Dependence of the Absorbance of the Solution on the Time in the Case of the Catalytic Reaction. NH_4VO_3, $3\times 10^{-5}M$; PHEN, $1\times 10^{-3}M$; oxine, $1\times 10^{-3}M$; $KClO_3$, $1,4\times 10^{-2}M$; pH 2,0; t° 17,0°C.

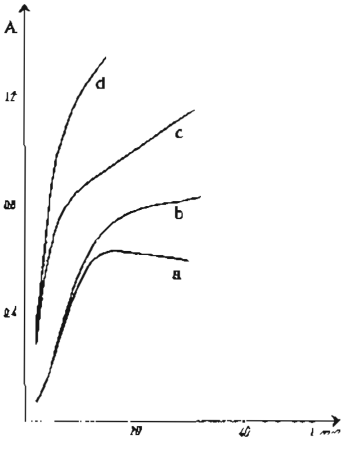

Figure 4. Dependence of the Absorbance of the Solution on the Time at Different Chlorate Concentrations. NH_4VO_3, $3\times 10^{-5}M$; PHEN, $1\times 10^{-3}M$; oxine, $1,5\times 10^{-3}M$; pH 2,0; (a) $KClO_3$, $4,0\times 10^{-2}M$; t° 17,0°C; (b) $KClO_3$, $7,2\times 10^{-2}M$; t° 17,0°C; (c) $KClO_3$, $4,0\times 10^{-7}M$; t° 40,0°C; (d) $KClO_3$, $7,2\times 10^{-2}M$; t° 40,0°C.

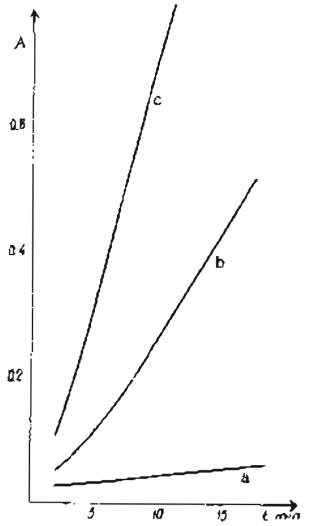

Figure 5. Dependence of the Absorbance of the Solution (a) in the absence of NH_4VO_3; (b) NH_4VO_3, $2\times 10^{-7}M$; (c) NH_4VO_3, $5\times 10^{-7}M$.

The course of the curves b, c in Figure 5 shows that in the presence of bromate rate determining stage of the catalytic reaction becomes again the formation of the charge transfer complex [ox-V^V-PHEN]. In such a way the sensitivity of the catalytic reaction could be increased in a considerable extent. That fact could be used for high sensitive catalymetric determination of microamounts of vanadium.