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Catalytic Activity and Complexation. II. Complex Agents, Affecting the Entrance of the Substrate into the Coordination Sphere of the Catalyst[1]

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8-hydroxyquinoline (oxine) is one of the first known activators for homogeneous catalytic processes in solutions. The mechanism of its action, however, remained unknown till now. In the present work the influence of oxine and its derivatives on the reaction kinetics of a model catalytic reaction was studied. The oxidation of p-phenetidine hydrochloride with chlorate, catalysed by vanadium(V) was used as a model reaction. It was shown, that oxine increases in a high extent the reaction rate, affecting the formation of a charge transfer complex between the catalyst and the organic substrate. The acceleration of the process is explained on the basis of the strong π-trans effect of oxine, which thus favours the substrate to enter the coordination sphere of the catalyst.

Introduction

It was yet shown that the introducing of some complexing agents during the course of homogeneous catalytic reactions could increase in a high extent the reaction rate.[2] The action of such an activator could be due to its oxidation to free radicals in the reaction course,[3] to its influence on the effective charge of the metal ion catalyst,[1] to its role as mediator in the process of electron transfer between the catalyst and the substrate[4] or to some other reasons.[2]

The present work is dedicated to another type of activation, where the activator helps the entrance of the substrate in the coordination sphere of the catalyst. The oxidation of p-phenetidine hydrochloride (PHEN) with chlorate, catalysed by vanadium(V) was used as a model reaction. The effect of oxine and its derivatives as activators for the process was studied.

Experimental Section

The choice of the model reaction was based on the earlier investigations of p-phenetidine catalytic oxidation. The mechanism of this process is yet well known—the role of the catalyst in it estimated[5] as well as the intermediate and final products.[6]

A photometric method was used to follow the kinetics of the reaction because the reaction products are intensively coloured. The glass reaction vessel with three sections[5] containing the reagents was placed in a thermostat for 15 minutes. The reagents were then mixed by vigorous shaking and the solution was placed in the cell of the photometer FEK-M, equipped with a device for constant temperature regulation. The absorbancy A of the solution was followed for a period of some 10-15 minutes. In the initial period of the reaction, when the reacted part x of the reagents is small compared to their original concentrations C_o the kinetic equation

$$\frac{dx}{dt} = k\,(C_o - x) \qquad (1)$$

could be simplified to

$$\frac{dx}{dt} = k\,C_o \qquad (2)$$

If equation (2) is combined with Bouguer-Lamber-Beer law, it takes the form

$$\frac{dA}{dt} = k'\,C_o \qquad (3)$$

Equation (3) shows that the apparent rate constant k′ could be determined from the slope dA/dt of the graph of absorbancy A against the time t.

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

During the course of the reaction the acidity was kept constant by means of buffer solutions, prepared from phosphoric, boric, acetic acids and sodium hydroxide.

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(1) Part I. P. R. Bontchev and V. Michaylova, *J. Inorg. Nucl. Chem.*, 29 (1967), in press.
(2) P. R. Bontchev and K. B. Yatzimirskii, *Theor. Exp. Chem.*, *1*, 180 (1965).
(3) P. R. Bontchev and K. B. Yatzimirskii, *Z. Fiz. Chim.*, 39, 1995 (1965); P. R. Bontchev and A. A. Alexiev, *Ukrain. Chem. J.*, 32, 1044 (1966).
(4) P. R. Bontchev, G. St. Nikolov and B. Lilova, *Ann. Univ. Sofia*, 59, 87 (1964/65).
(5) P. R. Bontchev and B. G. Jeliazkowa, *Mikrochim. Acta*, Wien, 125 (1967).
(6) P. R. Bontchev and B. G. Jeliazkowa, *Mikrochim. Acta*, Wien, 116 (1967).

Results and Discussion

The catalytic oxidation of PHEN by chlorate and V(V) as a catalyst does not proceed in a measurable extent at 20°C when the concentrations of the reagents are as follows: PHEN $1 . 10^{-3}M$, $KClO_3$ $8 . 10^{-3}M$, NH_4VO_3 $3 . 10^{-5}M$. The formation of coloured products could be observed at higher concentrations of the catalyst or the reagents, or if the temperature is higher (60-70°C). When oxine is present in the solution even at low concentrations ($5 . 10^{-4}M$) a strong violet coloration developed in a short time. The absorption spectra of the solution during the course of the reaction show that first a coloured substance I, with absorption maximum at $\lambda_{max} = 552$ mμ is formed, which then slowly turns into another coloured compound II with $\lambda_{max} = 510$ mμ1 (Figure 1).

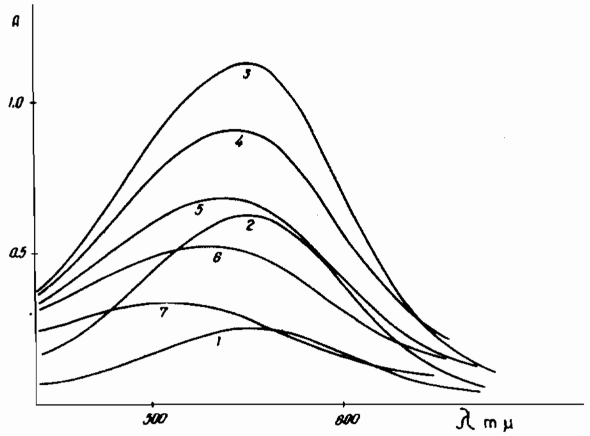

Figure 1. Absorption Spectra of the System Oxine-p-Penetidine-Vanadium(V) in the Course of the Reaction. The spectra are registered at different periods of time after the mixing of the reagents: 1, 11 min; 2, 22 min; 3, 50 min; 4, 72 min; 5, 95 min; 6, 118 min; 7, 164 min. The concentration of all the reagents is $2 . 10^{-4}M$; pH 2; t° 20°C; cell length, 50 mm; spectrofotometer SF-10.

The coloured substance I is a complex compound of vanadium(V) and not an oxidation product of PHEN. It is not extracted by the usual organic solvents, decolorizes in the presence of excess of EDTA and other complexing agents, can be completely sorbed on strongly acidic cationites as Dowex-50 and KPS-200. The absorption spectrum of the substance I in the visible region is identical with the spectrum of the charge transfer complex, formed between vanadium(V) and PHEN, when the latter is oxidized in the presence of the catalyst V(V).[5] The substance I and the charge transfer complex could be extracted with chloroform in the presence of solid sodium perchlorate. The absorption spectra of their neutral forms in the visible region were compared and found to be identical too.

The compound II was identified as the final product of the catalytic oxidation of PHEN i.e. N-(4-ethoxyphenyl)-quinonimine.[6] Its identity was confirmed also by means of elementary analysis data.

Figure 1 permits to estimate roughly the molar extinction coefficient ε of the charge transfer complex, because the value of ε of N-(4-ethoxyphenyl)-quinonimine was found before[6] to be 5,8 . 10^3. If we assume that the charge transfer complex is completely formed when the maximal absorbancy at $\lambda = 552$ mμ is obtained, that given 8,7 . 10^3 as a lowest possible value for the molar extinction coefficient of the complex (the amount of quinonimine formed during this period of time being neglected).

The coloured substances, formed during the course of the reaction show, that the presence of oxine does not affect the mechanism of the reaction which in general remains unchanged. We have already shown[5] that when PHEN is catalytically oxidized, first a charge transfer complex (CTC) is formed between the catalyst and the substrate, in which then a complete transfer of electron proceeds. As a result PHEN is oxidized to the coloured product P and vanadium(V) reduced to vanadium(IV). The latter is oxidized by chlorate and thus returns in the reaction cycle:

$$V(V) + PHEN \rightleftarrows [V(V) - PHEN] \qquad (4)$$

$$[V(V) - PHEN] \rightarrow P + V(IV) \qquad (5)$$

$$V(IV) + ClO_3^- \rightarrow V(V) + Cl^- \qquad (6)$$

The rate limiting stage of the reaction is the formation of CTC (the process (4)). It might be expected, therefore, that oxine, which increases the overall reaction rate, affects this stage of the reaction. The experiments confirmed this assumption and showed that the complex formation rate increases many times in the presence of oxine. For that reason the influence of oxine on the formation of the charge transfer complex with $\lambda_{max} = 552$ mμ was investigated in details.

The reaction system in this case contained only ammonium metavanadate, PHEN and oxine. The experiments were carried out at 20°C in order to prevent further fast oxidation in CT complex. The reagents were present in 1:1:1 ratio, their concentrations being $2 . 10^{-4}M$ in all the experiments.

The influence of the acidity on the reaction rate was studied in the pH range 1,8-4,1. The results are represented on Figure 2, where the reaction rate data in the absence of oxine are also shown for comparison. As can be seen, oxine strongly affects the complex formation, its effect being higher at the lowest pH values (1,8 and 2,2). At higher pH values an appreciable amounts of CT complex between vanadium(V) and PHEN are formed and the effect of oxine on the process decreases.

The kinetics of the complex formation in a solution containing vanadium(V), PHEN and oxine was investigated at pH 1,8 and 2,2, all reagent concentrations being $2 . 10^{-4}M$. In this pH range and the reagent concentrations used no CTC is practically formed in the absence of oxine. The addition of oxine leads to a fast formation of large amounts of CTC. The rate of the next oxidation stage (5)—the formation of N-(4-ethoxyphenyl)-quinonimine is very slow at 20°C and the first appreciable amounts of it could be detected about 30 minutes after the mixing of the reagents. For that reason, in the reaction conditions shown above the ab-

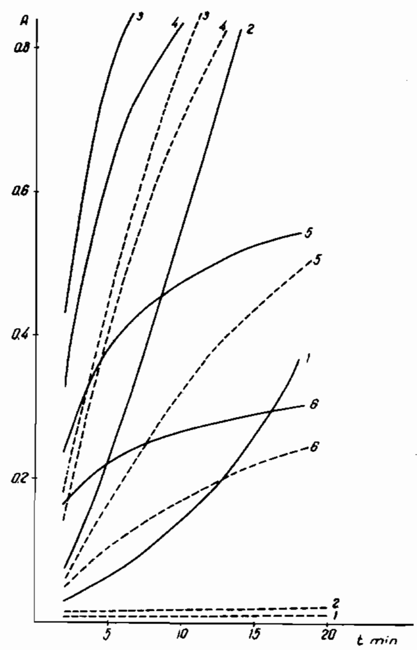

Figure 2. Dependence of the Absorbancy on the Time at Different pH Values. 1, pH 1,8; 2, pH 2,2; 3, pH 2,9; 4, pH 3,2; 5, pH 3,8; 6, pH 4,1; all reagent concentrations are $2 . 10^{-4} M$; t° 20,0°C; green filter with λ_{max} = 530 mμ; cell length, 50 mm; with dotted line are shown the corresponding values in the absence of oxine at the same reaction conditions.

sorbancy of the solution in the initial period of the reaction (15-20 min) could be used to study the process of the complex formation only. The course of the kinetic graph at these pH values shows (Figure 2, curves 1 and 2) that CTC concentration does not depend linearly on the time, but is proportional to t^2 (Figure 3). This fact indicates that the complex formation proceeds at least in two slow steps with comparable rates.

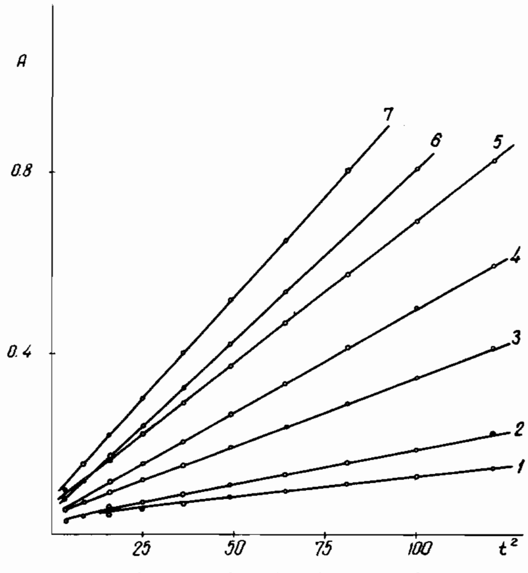

Figure 3. Dependence of the Absorbancy of the System Oxine-p-Phenetidine-Vanadium(V) on t^2. NH_4VO_3, $2 . 10^{-4} M$; oxine, $2 . 10^{-4} M$; PHEN: 1, $2 . 10^{-4} M$; 2, $4{,}0 . 10^{-4} M$; 3, $6{,}0 . 10^{-4} M$; 4, $8{,}0 . 10^{-4} M$; 5, $1{,}0 . 10^{-3} M$; 6, $1{,}2 . 10^{-3} M$; 7, $1{,}4 . 10^{-3} M$; pH 2,0; t° 17,0°C; green filter with λ_{max} = 530 mμ; cell length 50 mm.

It seems worth noting that analogous course of the A/t graphs is observed also during the CTC formation between vanadium(V) and PHEN only (Figure 4). The complex formation might proceed, for instance, during the formation of an outer-sphere complex [V(V),PHEN] as a first step of the process, followed then by the formation of the charge transfer complex [PHEN-V(V)].

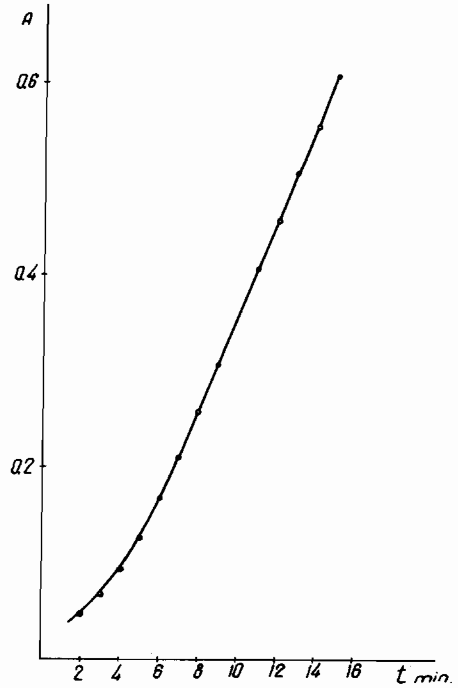

Figure 4. Dependence of the Absorbancy on the Time in the System p-Penetidine-Vanadium(V). PHEN, $9 . 10^{-4} M$; NH_4VO_3, $9 . 10^{-4} M$; pH 2,0; t° 17,0°C; green filter with λ_{max} = 530 mμ; cell length 50 mm.

We tried to estimate the sequence of the reagent interaction in the presence of oxine. For this purpose two of the reagents were thermostated together for 15 minutes and then mixed with the third one. The experiments, however, show the same course of the kinetic graphs A/t at each combination of the mixed reagents. This fact could mean only that the interaction of vanadium(V) with one of the reagents proceeds much faster than the next two stages of the reaction which determine the overall reaction rate. Thus, the kinetic investigations lead to the conclusion that the complex formation between vanadium(V) and PHEN in the presence of oxine proceeds in three steps—first one, interaction of V(V) with one of the other reagents, which is the fastest step, and then, two other steps with comparable rates.

It is seen from Figure 2 that at pH 2 and reagent concentrations $2 . 10^{-4} M$ there is no detectable interaction between V(V) and PHEN. On the other hand it is well known that vanadium(V) easily reacts with oxine even at pH 2.[7] It might be suggested, therefore, that the interaction between V(V) and oxine is the first, fastest stage of the process. The addition of PHEN to that complex proceeds in two steps, which can be

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(7) J. Stary, *Analyt. Chim. Acta*, *28*, 132 (1963).

formation of an outer-sphere complex between oxine-V(V) species and PHEN, and then – a partly electron transfer PHEN→V(V) and formation of CT complex.* The three steps of the process can be represented as follows :

$$V(V) + ox \overset{K_1}{\rightleftarrows} [ox\text{-}V(V)] \quad \text{fast} \qquad (7)$$

$$[ox\text{-}V(V)] + PHEN \overset{K_2}{\rightleftarrows} [ox\text{-}V(V),PHEN] \quad \text{slow} \qquad (8)$$

$$[ox\text{-}V(V),PHEN] \overset{K_3}{\rightleftarrows} [ox\text{-}V(V)\text{-}PHEN] \quad \text{slow} \qquad (9)$$

where K_1, K_2 and K_3 are the corresponding equilibrium constants. The equations (8) and (9) are thought to be shifted to right, *i.e.* it is assumed for the corresponding rate constants that $k_2 \gg k_{-2}$ and $k_3 \gg k_{-3}$.

Introducing the abbreviations $[ox\text{-}V(V)] = B$, $[ox\text{-}V(V),PHEN] = C$ and $[ox\text{-}V(V)\text{-}PHEN] = D$ we obtain from (7), (8) and (9) the kinetic equations:

$$\frac{d[C]}{dt} = k_2 \,.\, [B] \,.\, [PHEN] - k_3 \,.\, [C] \qquad (10)$$

$$\frac{d[D]}{dt} = k_3 \,.\, [C] \qquad (11)$$

where k_2 and k_3 are the corresponding rate constants.

For the initial period of the reaction, when $[C] \ll [B]$, and $[D] \ll [C]$ we can consider [B] and [PHEN] as constants. The solution of (10) in this case leads to the equation

$$[C] = k_2 \,.\, [B] \,.\, [PHEN] \,.\, t \qquad (12)$$

which combined with (11) gives

$$\frac{d[D]}{dt} = k_2 \,.\, k_3 \,.\, [B] \,.\, [PHEN] \,.\, t \qquad (13)$$

[B] can be determined from (7) and introduced in (13):

$$\frac{d[D]}{dt} = \frac{k_2 \,.\, k_3}{K_1} \,.\, [V(V)] \,.\, [ox] \,.\, [PHEN] \,.\, t \qquad (14)$$

The integration of (14) for the initial period of the reaction leads to the expression:

$$[D] = k \,.\, [V(V)] \,.\, [ox] \,.\, [PHEN] \,.\, t^2 \qquad (15)$$

The linear dependence of [D] on t^2 (Figure 3) is in a good agreement with equation (15) and thus—with the reaction mechanism shown above. For further experimental inspection of equation (15) the dependence of CTC concentration on the concentration of each one of the reagents was investigated.

For this purpose the function d[D]/dt was followed with increasing concentration of every one of the reagents. The function d[D]/dt in equation (14) was determined by a graphical method from the curve of absorbancy on the time in a point corresponding to the eighth minute from the start of the reaction.

Figure 5 shows that the dependence of d[D/]dt on [PHEN] has in fact a linear course as might be expected from equation (14). The same course was estimated also for the dependence of d[D]/dt on vanadium(V) and oxine concentrations.

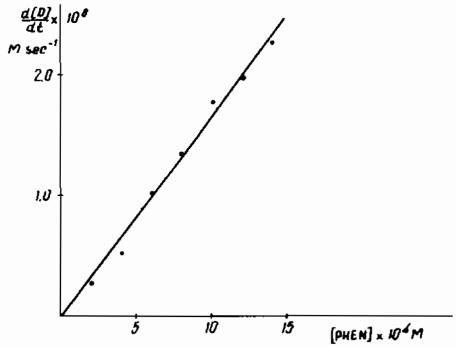

Figure 5. Dependence of d[D]/dt on PHEN Concentration. NH_4VO_3, $2 \,.\, 10^{-4}M$; oxine, $2 \,.\, 10^{-4}M$; pH 2,0; t° 17,0°C; 8 minutes after the mixing of the reagents.

It is necessary to discuss also the known data about the forms in which the reagents are present in the solution. The data for oxine[8] and PHEN[9] show, that even in slightly acid solutions they are present in the protonated forms Hox^+ (pK = 5,10) and $ArNH_3^+$ (pK = 5,25). As to vanadium(V), the data summarized in the paper of Schiller and Thilo[10] permit to conclude that in the pH range studied and at the low concentrations of V(V) used vanadium is present as VO_2^+, HVO_3 and VO_3^-. The V_{10}-polymer forms, so typical for vanadium in that range of acidity do not exist at such dilution (V(V) concentration is about $10^{-4}M$). We used the data given in [10] to draw up the diagram for the forms of vanadium(V) in slightly acid solutions (Figure 6).

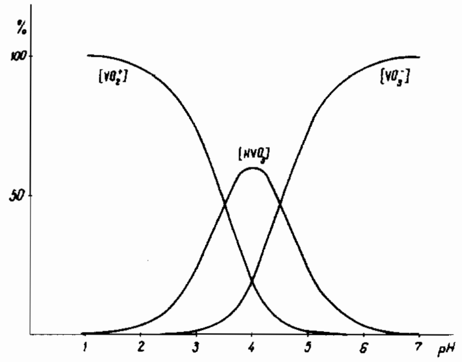

Figure 6. Diagram of the Vanadium(V) Forms in Slightly Acid Medium at Low Vanadium(V) Concentrations.

(*) The formation of outer-sphere complexes proceeds with a rate, which usually is higher than those observed for the second stage of the process. However, it is difficult to suppose any other explanation for the character of this stage of the reaction.

(8) E. B. Sandell, Colorimetric Determination of Traces of Metals. New York, Intersc. Publ., 3rd Ed., p. 185 (1959).

(9) A. Albert and E. Sergeant, Ionisation Constants of Acids and Bases, (in Russ.), Moscow: *Izdat. Chimia*, p. 139 (1964).

(10) K. Schiller and E. Thilo, *Z. anorg. Chem.*, *310*, 261 (1961).

Fig. 6 shows that at pH ~2 and the low concentrations used vanadium(V) is present mainly as VO_2^+ ion. This fact accounts for the negligible rate of interaction with the protonated form of PHEN—$ArNH_3^+$, the two reactants being of the same charge. In this pH range the effect of oxine on the CTC formation is maximal. It is not clear, however, why the interaction of VO_2^+ with Hox^+ proceeds fast. It is possible that the fact is analogous to that estimated by Diebler[11] who found that Cu^{2+} reacts fast with bipyridine in conditions where the latter exists mainly as $HBipy^+$. The rate constant for the reaction between the unprotonated form Bipy and Cu^{2+} is however several orders of magnitude higher than the one for the reaction $Cu^{2+} + HBipy^+$. For that reason a considerable part of the reaction proceeds via $Cu^{2+} + Bipy$ path, despite the very small amounts of the unprotonated form. The experimental fact of fast interaction between Hox^+ and VO_2^+ needs however a more detailed examination in order to clear its mechanism.

When the pH increases till 3,2-3,5 the rate of CTC formation becomes too high and the effect of oxine is not so large—the reaction proceeds mainly by a pattern without the participation of oxine. For that reason in this pH range the course of the A/t graphs in the presence of oxine (Figure 2) shows no signs of many stages in the complex formation. The formation of CTC in the absence of oxine in this pH range shows that probably the CTC is formed from HVO_3 and $ArNH_3^+$.

The decrease in complex formation at higher pH values and the positive charge of the CT complex as well indicate to the lack of interaction between VO_3^- and $ArNH_3^+$, in spite of the different charges of the reactants.

We consider that the presence of oxine in the coordination sphere of vanadium(V) can accelerate the CTC formation by the folowing reasons:

The free π*-orbitals of oxine make it a strong electron acceptor—it easily forms π (M→L) bonds with many metal ions of the transition series.[12] The dative π (M→L) bonds in these complexes account for the *π-trans* effect of oxine and its derivatives.

In moderately acid solutions and low concentrations ($10^{-4}M$) vanadium(V) exists mainly as aquated VO_2^+ ion.* In VO_2^+ vanadium(V) has its vacant d-orbitals partly populated, due to the oxygen atoms on the z-axis and water molecules in the xy-plane. For that reason in VO_2^+ ion there is an appreciable electron density on the d-orbitals of vanadium and the formation of π (M→L) bonds with the participation of VO_2^+ becomes possible.

When 1:1 complex with oxine is formed, an electron density is delocalized from VO_2^+ to oxine as a result of interaction between the unoccupied π*-orbitals of oxine with the d-orbitals of vanadium. It might be expected for that reason that in the 1:1 complex V(V)-ox the bonds V(V)-H_2O are labilized and the displacement of water molecules by PHEN would proceed easier. The coordinated oxine molecule takes up a part of the excess electronic charge brought to vanadium by PHEN and lowers the overall activation energy. Thus, the physical significance of the oxine activation could be reduced to its strong *π-trans* effect in the complex with the catalyst.

When a large excess of oxine is present in the solution, 1:2 complex with the catalyst begins to form. In this compound the oxine molecules occupy the four places in xy-plane of VO_2^+ ion. Thus the coordination sphere of the catalyst is blocked up and it could not take further any part in the reaction; as a result the reaction rate begins to decrease.

The electron acceptor properties of oxine could be changed by means of suitable substituents in its molecule. Burton and Davis calculated the effective charges in the molecules of oxine and some of its derivatives.[13] They show, that the transition of oxine in excited state (π—π*) favours the formation of π (M→L) bonds in its chelates because the excited form of oxine is a better electron acceptor. The bonding of the nitrogen atom of the heterocycle with a metal ion facilitates the transition (π—π*) in the molecule and thus—the formation of dative π (M→L) bonds as well. The transition (π—π*) is favoured also by halogen atoms in the phenolic ring of the oxine molecule; alkyl and aryl substituents in the heterocycle act in the opposite direction. We used some oxine derivatives and some pyridines in order to verify the corelation between the electron acceptor properties and the effect of activation. The results are given in Table I.

Table I. Rate of CTC Formation in the Presence of Different Activators

Activator	$\frac{dA}{dt}$
7-iod-8-hydroxyquinoline-5-sulfonic acid	$8{,}70 \,.\, 10^{-1}$
8-hydroxyquinoline	$2{,}40 \,.\, 10^{-2}$
2-methyl-8-hydroxyquinoline	$0{,}08 \,.\, 10^{-2}$
pyridine	$0{,}05 \,.\, 10^{-2}$
2-methyl-pyridine	$0{,}04 \,.\, 10^{-2}$
4-amino-pyridine	$0{,}03 \,.\, 10^{-2}$
without activators	$0{,}04 \,.\, 10^{-2}$

NH_4VO_3, $2 \,.\, 10^{-4}M$; PHEN, $2 \,.\, 10^{-4}M$; activator, $2 \,.\, 10^{-4}M$; pH 2,0; t° 17,0°C.

As it is seen from Table I, 7-iodo-8-hydroxyquinoline-5-sulfonic acid shows very high activation effect, due to the presence of iod in the phenolic ring, when 2-methyl-8-hydroxyquinoline has practically no effect on the reaction rate. The lack of activation when 2-methyl-8-hydroxyquinoline is used might be due to steric reasons also—the methyl group in α-position to the heterocyclic nitrogen has a hindrance effect and the formation of a chelate compound would be more difficult.[1] In the cases when pyridine compounds are used there is also no possibility for a chelate formation and therefore for any activating effect.

Perkampus and Kortüm had shown that solvents with low polarity favour the formation of dative π (M→L) bonds in oxine complexes.[14] We try to use

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(11) H. Diebler, EUCHEM Conference on Inorg. Mechanisms, Kinsale, Ireland (1967).

(12) L. Morpurgo and R. J. P. Williams, *J. Chem. Soc.*, (A), 73 (1966).

(*) For some other possibilities of the structure of this ion see H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4411 (1962).

(13) R. E. Burton and W. J. Davis, *J. Chem. Soc.*, 1766 (1964).

(14) H. H. Perkampus and K. Kortüm, *Z. analyt. Chem.*, *190*, 111 (1962).

this possibility in order to increase further the activating effect. The influence of CH_3OH, C_2H_5OH and i-C_3H_7OH on the reaction rate was studied in the presence of oxine. It was shown, that the change of water as a medium with 1:1 alcohol-water solution increases the reaction rate about 15 times. This fact also supports the view for the role of π (M→L) bond formation in the activating effect of oxine.

In the presence of oxine the process (6) also proceeds in a different way. When the oxidation of PHEN by V(V) takes place in the complex [ox-V(V)-PHEN] the catalyst after its reduction remains bound in a complex with oxine. Hence, in the presence of oxine the processes (5) and (6) must be represented as:

$$[\text{ox-V(V)-PHEN}] \rightarrow \text{P} + [\text{ox-V(IV)}] \qquad (16)$$

and

$$[\text{ox-V(IV)}] + ClO_3^- \rightarrow [\text{ox-V(V)}] + Cl^- \qquad (17)$$

Obviously, the rates of (17) and (5) would be different and on the basis of general considerations only it could not be predicted which of them would be higher. However the known data show[15] that vanadium(IV) bound in complexes with strong electron acceptors is readily oxidized to vanadium(V). The complex of V(IV) with oxine, for example, is easily oxidized by air even in acid solutions.[15] On that reason we assume that probably the oxidation of [oxine-V(IV)] by chlorate proceeds faster than the process (6). This assumption, however, needs further experimental verification.

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(15) J. Selbin, *Chem. Revs.*, 65, 160 (1965).