AUTOOXIDATION OF HYDROXYLAMINE CATALYSED BY COBALT(II) TETRASULPHOPHTHALOCYANINE. MODELS OF OXIDASES

D. M. WAGNEROVÁ, E. SCHWERTNEROVÁ and J. VEPŘEK-ŠIŠKA

Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6

Received September 21st, 1973

Oxidation of hydroxylamine by molecular oxygen, similar to the oxidation of hydrazine, is catalyzed by cobalt(II) tetrasulphophthalocyanine (CoTSP). The oxidation products are nitrogen, dinitrogen oxide and nitrite. Oxygen is reduced to water and hydrogen peroxide, whose reaction with hydroxylamine and/or hydrazine is also catalysed by CoTSP.

The kinetics of the reactions catalysed by CoTSP obey the Michaelis–Menten equation. The mechanism of these reactions can best be explained by the formation of a ternary complex (substrate–catalyst–oxidant), in whose coordination sphere occurs the actual electron transfer without liberation of free radicals from the complex.

Autooxidation of hydrazine catalysed by Co(II) tetrasulphophthalocyanine[1] (CoTSP) has demonstrated the relation between the catalytic properties of a catalyst and its ability to bind reversibly molecular oxygen. The study of oxidation of another substrate containing the nitrogen donor allows us to generalize some conclusions on the catalytic properties of CoTSP, whose action is a simplified model of the function on an oxidase. Autooxidation of hydroxylamine, described in the present paper, has a more complex mechanism than autooxidation of hydrazine. It is a non-complementary reaction, which may give rise to several products of different oxidation degrees. In addition, a prerequisite for the formation of nitrogen and dinitrogen oxide as reaction products is the formation of a multiple bond between nitrogen atoms.

EXPERIMENTAL

Cobalt(II) 4,4′,4″,4‴-tetrasulphophthalocyanine was prepared according to a described procedure[2]. Sodium hydroxide (Merck), hydroxylamine hydrochloride and the other chemicals were of A.G. purity.

Apparatus and Procedure

Concentration of oxygen was followed polarographically, at a constant potential $-0{\cdot}7$ V (SCE). An apparatus LP 55 with a recorder EZ 2 was employed. The initial concentration of oxygen was given by its solubility in the reaction medium (c. $2{\cdot}5 \cdot 10^{-4}$M). Calibration was made with $0{\cdot}1$M and 1M solutions of KCl. The reaction was conducted mostly in a borax buffer, pH range 10·0 to 12·3, the catalyst concentration being 5 . 10^{-8} to 5 . 10^{-6}M.

The reaction was studied in a polarographic vessel with a water jacket thermostated to 25·0 ± ± 0·1°C. The vessel was equipped with a side tube with mercury, by which the level of the solution could be raised up to the stopper of the vessel. In this way the dead space over the level was eliminated. The component starting the reaction or gaseous nitrogen was brought to the solution by means of a hypodermic needle, inserted through the stopper.

The reaction of hydrogen peroxide with hydroxylamine proceeded under the same conditions as the autooxidation. Prior to an experiment the solution was bubbled with nitrogen, which had been freed from oxygen by being passed through a solution of chromous chloride and an alkaline solution of hydrazine and CoTSP. The concentration of hydrogen peroxide was measured polarographically at a constant potential of −1·6V (SCE). In determining the concentration of hydrogen peroxide in the course of the autooxidation the reaction was stopped at a chosen time by the addition of sulphuric acid, the solution was bubbled with nitrogen and hydrogen peroxide was determined. In all experiments the reaction mixture contained 8 . 10^{-4}M-EDTA, to eliminate the catalytic effect of trace impurities.

The gaseous reaction products were analysed by a gas chromatograph Chrom III (Laboratorní přístroje). In the reaction of hydrogen peroxide with hydroxylamine nitrogen and dinitrogen oxide were separated on active carbon and detected with a catharometer. The carrier gas was hydrogen. Samples were taken at a steady course of the reaction.

Absorption spectra of the solutions were recorded with a spectrophotometer Pye Unicam SP 800 B. The formation of a CoTSP-substrate complex in an anaerobic medium was demonstrated by the continuous variation method. The solutions were prepared directly in a closed cell, into which nitrogen or another reaction component was brought by a syringe needle. Oxygen was removed from the solution by nitrogen bubbled through at 70°C. The absorbance of the formed complex was measured at a wave length of 450 nm.

Nitrite was determined colorimetrically after a diazotization reaction with sulphanilic acid and α-naphthylamine.

RESULTS AND DISCUSSION

Kinetics of the Oxidation of Hydroxylamine

The oxidation of hydroxylamine by molecular oxygen in the presence of CoTSP as catalyst occurred only at pH > 10. In the absence of CoTSP and the presence of EDTA, under the same conditions, the reaction rate was practically zero.

At pH 11·6 to 12·3 and initial hydroxylamine concentrations 1 . 10^{-4} to 2·5 . . 10^{-3}M the instantaneous concentration of oxygen as a function of time corresponded to no simple reaction order. For this reason the reaction course is described by the method of initial reaction rate, v_0, where the effect of consecutive reactions is avoided. The value of v_0 was determined graphically as a tangent to the curve relating the instantaneous concentration of oxygen to time. In Fig. 1 the quantity v_0 is plotted *vs* the starting concentration of hydroxylamine for three starting concentrations of oxygen. The curve fits the Michaelis-Menten equation[3]

$$v_0 = kK[\text{CoTSP}]\,[\text{NH}_2\text{OH}]/(1 + K[\text{NH}_2\text{OH}])\,. \qquad (1)$$

In a series of experiments with the same starting concentration of oxygen the value of v_0 was deterimend at a practically constant concentration of oxygen, included in the rate constant k. The validity of the Michaelis-Menten equation for the given system was verified by graphical linearization of equation (*1*), *i.e.* by plotting $1/v_0$ *vs* $1/[NH_2OH]$ and $v_0/[NH_2OH]$ *vs* v_0. In this way also the experimental constants k and K, listed in Table I were determined.

The relation of v_0 to the catalyst concentration at pH 12·3 was linear in the range $5 . 10^{-8}$ to $5 . 10^{-6}$M CoTSP.

The initial reaction rate, v_0, steeply increased with pH in the pH range 11·6 to 12·3. At pH 11·6 the reaction was very slow and at pH < 10 the reaction rate was practically zero. Similar observations were reported with other reactions of CoTSP and it has been assumed that a prerequisite for the reactivity of CoTSP is dissociation of a very weakly acidic hydrogen atom, probably from the pyrrol nitrogen of the phthalocyanine, whose pK should be[4] approximately 12. Consequently, if the concentration of the reactive, deprotonized form of CoTSP is expressed in terms of the equilibrium constant K_d and mass balance, equation (*1*) takes the form

$$v_0 = \{k \, . \, K \, . \, K_d[NH_2OH] \, [CoSTP]_a/(1 + K[NH_2OH])\} \, . \, 1/(K_d + [H^+]) \, . \tag{2}$$

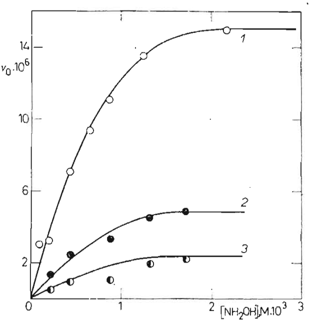


FIG. 1

v_0 *vs* $[NH_2OH]$ for 3 Initial Concentrations of Oxygen (Michaelis-Menten equation)

pH 12·3; $2·6 . 10^{-6}$M-CoTSP; 25°C; $[O_2]$ *1* $2·5 . 10^{-4}$M; *2* $1·55 . 10^{-4}$M; *3* $0·85 . 10^{-4}$M.

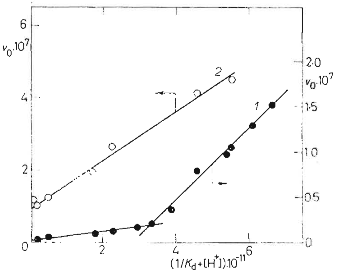


FIG. 2

v_0 *vs* $(K_d + [H^+])^{-1}$ for $K_d = 1 . 10^{-12}$

$8.62 . 10^{-4}$M-NH_2OH; $4·3 . 10^{-6}$MCoTSP, 25°C; *1* $NH_2OH + O_2$; *2* $NH_2OH + H_2O_2$, In this series of experiments the starting concentration of hydroxylamine was constant, so that equation (*2*) could be linearized. The dependence of the experimental values of v_0 on $1/(K_d + [H^+])$ for the assumed value of $K_d = 1 . 10^{-12}$ is drawn in Fig. 2 (curve *1*) and shows agreement with equation (*2*) in the region of the steep increase of reaction rate with pH.

Analysis of the reaction products has revealed that autooxidation of hydroxylamine gives rise to nitrogen, dinitrogen oxide and nitrite. Polarography of the reaction mixture detected the formation of hydrogen peroxide, as intermediate in the reduction of oxygen, and a decrease of its content with time. This decrease was due either to decomposition of hydrogen peroxide or to its reaction with hydroxylamine. Either reaction might be catalysed by CoTSP. In order to decide between the two possibilities the behaviour of hydrogen peroxide was the subject of a separate study.

Oxidation of hydroxylamine by hydrogen peroxide. It was found that in a borax buffer of pH 11·5 to 12·3 containing $5 . 10^{-7}$ to $1 . 10^{-4}$M CoTSP and $8 . 10^{-4}$M EDTA no decomposition of hydrogen peroxide occurred. In the absence of EDTA the peroxide decomposed, but the decomposition rate was little influenced by concentration of CoTSP, which, consequently, did not catalyse the decomposition. The data on the catalytic effects of CoTSP, FeTSP and MnTSP upon the decomposition of hydrogen peroxide[5] were obtained in the absence of EDTA and at catalyst concentrations higher by two orders of magnitude. It appears that the observed catalytic effects were probably due to free metallic ions, present in the substance as impurities.

Oxidation of hydroxylamine by hydrogen peroxide was catalysed by CoTSP. The kinetics of the catalysed oxidation of hydroxylamine were investigated under the same conditions as the kinetics of its autooxidation; the concentration of hydrogen peroxide was followed polarographically. The dependence of v_0 on the initial concentration of hydroxylamine at a constant initial concentration of hydrogen peroxide, $2·44 . 10^{-4}$M, also obeyed the Michaelis-Menten equation. The rate constant and the

TABLE I

Rate and Equilibrium Constants of the Reactions Studied pH 12·3; $[O_2] = 2·5 . 10^{-4}$M; 25°C

k Experimental rate constant, K-Michaelis equilibrium constant, k_1-rate constant of the rate-determining step, K_2-stability constant of the ternary complex.

Reaction	k $s^{-1}\,M^{-1}$	K	k_1 s^{-1}	K_2
$NH_2OH + O_2$	9·15	$1·21 . 10^3$	25·0	$2·0 . 10^3$
$NH_2OH + H_2O_2$	0·13	$3·0 . 10^3$	—	—
$N_2H_4 + O_2$	1·15	$4·5 . 10^3$	—	—

equilibrium constant calculated from the equation are given in Table I. It is seen that the kinetic course of the oxidation by hydrogen peroxide and of the autooxidation are the same, but the rate of the former is about one seventieth of the rate of the latter.

The dependence of v_0 upon the concentration of hydrogen ions is plotted in Fig. 2 (curve 2); it shows that equation (*2*) is applicable even to oxidation of hydroxylamine by hydrogen peroxide. This is consistent with the assumption that the character of the dependence is controlled by the acidobasic properties of CoTSP.

Products of the autooxidation. To be able to elucidate the mechanism of the autooxidation it was necessary to have data on the proportion of the products or intermediates and to know their dependence upon the reaction conditions. The change of the concentration of hydrogen peroxide with time suggests that at the start of the reaction the concentration of hydrogen peroxide rapidly increases up to a maximum, attained in 60 to 100 seconds. The ratio of the formed hydrogen peroxide to the consumed oxygen shows that in the first few seconds of the reaction 90 to 95% of the consumed oxygen is reduced to hydrogen peroxide only. This value rapidly drops to 30–50%, which means that the portion of oxygen reduced to water increases (Fig. 3). The subsequent reaction of hydrogen peroxide with hydroxylamine manifests itself much later.

Parallel determination of hydrogen peroxide and nitrite in the same sample (on stopping the reaction) demonstrated validity of the equation $[H_2O_2] = \Delta O_2 - [NO_2]$, (3) where ΔO_2 is the decrease in the content of oxygen. The determination refers to an initial hydroxylamine concentration of $4{\cdot}4 \,.\, 10^{-4}$ to $4{\cdot}4 \,.\, 10^{-2}$M. The decrease in $[H_2O_2]$ caused by its reaction with hydroxylamine was allowed for. Equation (*3*) shows that that part of oxygen which is reduced to water is utilized for the oxidation

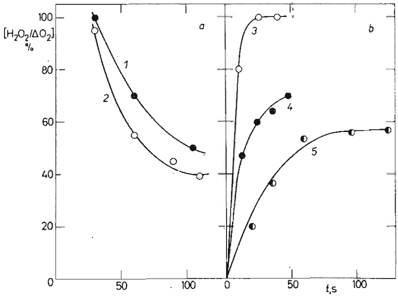


FIG. 3

$[H_2O_2]/\Delta O_2$ *vs* Time in the Autooxidations of NH_2OH and N_2H_4

pH 12·3; 25°C; [CoTSP] *1* $4{\cdot}3 \,.\, 10^{-6}$M; *2* $1{\cdot}76 \,.\, 10^{-6}$M; *3* $4{\cdot}3 \,.\, 10^{-6}$M; *4* $2.1 \,.\, 10^{-6}$M; *5* $0{\cdot}8 \,.\, 10^{-6}$M.

a NH_2OH, *b* N_2H_4.

of hydroxylamine to nitrite. If the oxidation of hydroxylamine to nitrite was accompanied by a limited formation of hydrogen peroxide it should hold that $[H_2O_2] > < \Delta O_2 - [NO_2^-]$.

Fig. 4 relates the concentration of nitrite to the intial concentration of hydroxylamine. The concentration of nitrite was determined at the end of the reaction (curves *3*, *4*) or on interrupting the reaction at its different stages (curves *1*, *2*). The nonlinearity demonstrates that with increasing concentration of hydroxylamine the relatitive portion of the formed nitrite decreases.

Analysis of the gaseous products of autooxidation of hydroxylamine detected a small quantity of dinitrogen oxide. In the reaction of hydroxylamine with hydrogen peroxide we found a ratio $N_2 : N_2O = 3 : 1$, the oxidation by hydrogen peroxide did not give rise to nitrite.

Oxidation of Hydrazine

The kinetics of the autooxidation of hydrazine catalysed by CoTSP were previously studied in the excess of oxygen[1]. Experiments performed under the same conditions as those in the autooxidation of hydroxylamine (pH 12·3, $[O_2] = 2{\cdot}5 \,.\, 10^{-4}$M, [CoTSP] $= 2{\cdot}6 \,.\, 10^{-6}$M, $[N_2H_4] = 2{\cdot}2 \,.\, 10^{-4}$ to $1{\cdot}75 \,.\, 10^{-3}$M, [EDTA] $= 8 \,.\, 10^{-4}$M) confirm that the reaction obeys the Michaelis-Menten equation. The constants determined from the dependence of v_0 on the starting concentration of hydrazine are given in Table I.

Autooxidation of hydrazine is a complementary reaction, so that it should occur in one step, with the formation of nitrogen and water. However, the presence of hydrogen peroxide in the reaction mixture suggests that the reaction may proceed by several reaction paths. Similarly as in the case of hydroxylamine it was observed that hydrogen

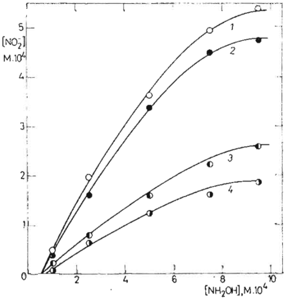


FIG. 4

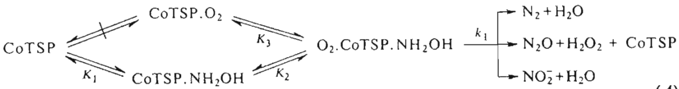
$[NO_2^-]$ *vs* the Initial Concentration of NH_2OH

pH 12·3; $2{\cdot}6 \,.\, 10^{-6}$M CoTSP; 25°C; *1*, *2* excess of O_2; *3*, *4* in a closed system.

peroxide oxidized hydrazine in the presence of CoTSP as catalyst. The consecutive reaction with hydrogen peroxide was also slower than the autooxidation; no decomposition of the peroxide was observed. In the course of the autooxidation of hydrazine the concentration of hydrogen peroxide was determined at different times of the reaction. The ratio of the formed peroxide to the consumed oxygen as a function of time is shown in Fig. 3. Its course is a reverse of that observed in the autooxidation of hydroxylamine – the higher the concentration of CoTSP, the greater the portion of oxygen reduced to peroxide. At $[\text{CoTSP}] \gtrsim 4 \cdot 10^{-6}\text{M}$ all oxygen was reduced to hydrogen peroxide. The main product of the autooxidation of hydrazine was found to be nitrogen. A trace of ammonia was also detected.

The Mechanism of Autooxidation

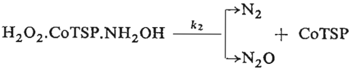
In the previous paper[1] it was demonstrated that the first step of the CoTSP-catalysed autooxidation of hydrazine is the formation of a ternary complex, and not the generation of free radicals $N_2H_4^{\bullet}$. The fundamental evidence in favour of this conclusion is valid even for the catalysed autooxidation of hydroxylamine: CoTSP reversibly forms binary adducts with oxygen and hydroxylamine. The existence of a CoTSP-hydroxylamine adduct, of a component ratio 1 : 1 and a stability constant $1{\cdot}5 \cdot 10^5$, has been demonstrated by the continuous variation method. Hence it is likely that in the presence of both components a ternary complex as an active intermediate is formed. The postulated complex complies with the conditions formulated by Siegel and coworkers[6,7]. According to these authors a ternary complex is substantially more stable than the starting binary complexes if a ternary complex contains N and O ligands, and at least one of the two ligands has the π-system, which may participate in the bond-formation (in our case phthalocyanine and O_2). Provided that the considered ternary complex is formed the autooxidation of hydroxylamine proceeds by the following mechanism:



(A)

As was shown previously[4], the equilibrium between CoTSP and CoTSP.O_2 is not sufficiently mobile, so that it cannot be considered. The rate of oxygen uptake by CoTSP is evidently dependent on the nature of the ligand in the trans position. A similar phenomenon was observed with heme, whose function is affected by the proximal histidine of globin[9]. The effect of the ligand can also be regarded as a variant of the so-called discrimination effect[6–8].

The subsequent reaction of hydrogen peroxide with hydroxylamine, whose kinetics are the same as the kinetics of autooxidation of the two substrates, can be interpreted by a mechanism analogous to (*A*):



$$H_2O_2.CoTSP.NH_2OH \xrightarrow{k_2} \left[\begin{array}{l} \rightarrow N_2 \\ \rightarrow N_2O \end{array}\right. + CoTSP \qquad (B)$$

At $t = 0$ the reaction rate is proportional to the concentration of the ternary complex

$$v_0 = -d[O_2]/dt = k_1[O_2.CoTSP.NH_2OH] \qquad (4)$$

After expressing its concentration by equilibrium constants K_1 to K_3 and considering mass balance we obtain

$$v_0 = \frac{k_1K_1K_2[CoTSP]\,[NH_2OH]\,[O_2]}{1 + K_1K_2/K_3[O_2] + K_1[NH_2OH] + K_1K_2[NH_2OH]\,[O_2]}\,. \qquad (5)$$

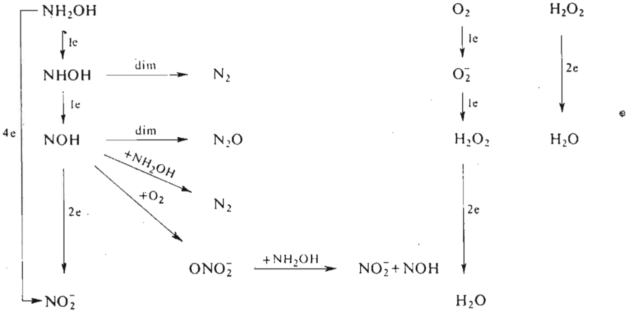
At a constant initial concentration of oxygen equation (*5*) is formally identical with the Michaelis-Menten equation, whose validity has been confirmed experimentally. The meanings of constants k and K are apparent from juxtaposition of equations (*1*) and (*5*):

$$k = k_1K_2[O_2]/(1 + K_2[O_2]) \qquad (6)$$

$$K = K_1(1 + K_2[O_2])/(1 + K_1K_2/K_3[O_2])\,. \qquad (7)$$

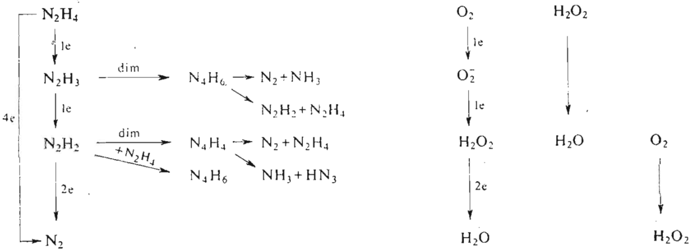
From the dependences of k and K on the initial concentration of oxygen we determined the real rate constant of hydroxylamine autooxidation, k_1, and the stability constant of the ternary complex, K_2. These constants, determined graphically by plotting k^{-1} *vs* $[O_2]^{-1}$, are given in Table I. The significance of the experimental constants determined for the autooxidation of hydrazine and the oxidation of hydroxylamine by hydrogen peroxide are given by equations of the same type as (*6*) and (*7*).

The conception of a ternary complex with oxygen and substrate in axial positions suggests that the first step of the oxidation process involves a transfer of four electrons. However, the transfer of the first or the first two electrons can either be followed by liberation of a free radical from the complex or the particle remains bound in the complex and participates in another electron transfer. The reaction scheme below shows the individual oxidation states of the substrate and oxygen, irrespective of whether they are free radicals or particles bound in the complex, and their possible consecutive reactions.



(*C*)

The release of a radical from the complex after the transfer of 1 or 2 electrons is, in fact, a hybrid mechanism involving the ternary complex and the free radical. The liberation of a radical from the complex is energetically disadvantageous, but is followed by ready dimerization (dim). If the particle remains in the complex the dimerization is sterically hindered, but another transfer of electrons within the complex is facile.



(*D*)

In the first case (liberation of radicals) the reaction mixture can be expected to contain a greater concentration of the dimerization product, *i.e.* N_2O. Nitrite may be formed, according to Hughes and Nicklin[10], by a radical reaction *via* a hypothetical peroxonitrite:

$$NO^{-\bullet} + O_2 \longrightarrow ONO_2^- \qquad (E)$$

$$ONO_2^- + NH_2OH + OH^- \longrightarrow NO_2^- + NO^{-\bullet} + 2\,H_2O \qquad (F)$$

According to reaction (*F*) the relative concentration of nitrite should increase with concentration of hydroxylamine, or remain practically unchanged if a concurrent reaction of nitroxyl with hydroxylamine takes place. At a low concentration of oxygen, *e.g.* towards the end of the reaction, dimerization of nitroxyl to N_2O, accompanied by an increase in the concentration of H_2O_2, should occur instead of the formation of peroxonitrite.

In the other case the oxidation within the ternary complex, without the liberation of a radical, should manifest itself by a low concentration of the dimerization product and by a rather high concentration of the product of the 4-electron reaction, *i.e.* nitrite. Molecular nitrogen would then be produced by reaction of the bound nitroxyl group

$$\mathrm{CoTSP.NOH} + \mathrm{NH_2OH} \longrightarrow \mathrm{N_2} + 2\,\mathrm{H_2O} + \mathrm{CoTSP} \qquad (G)$$

This reaction would discontinue the reduction of oxygen after a transfer of 2 electrons, and thus lead to the formation of hydrogen peroxide, and at the same time would compete with the formation of nitrite. Naturally, reactions (*E*) and (*F*) can be ruled out as impossible in the non-radical mechanism.

Experiment has revealed that the autooxidation of hydroxylamine produces a small amount of N_2O, as a dimerization product, but the content of nitrite attains as much as 60%. With increasing concentration of hydroxylamine the relative portion of the arising nitrite decreases, even in an excess of oxygen (Fig. 4). Hydrogen peroxide is formed mainly at the early stage of the reaction (Fig. 3). Both these facts are consistent with the second, non-radical alternative and with the concurrent reaction (*G*) at higher concentrations of hydroxylamine, but inconsistent with reactions (*E*) and (*F*).

The first mechanism, postulating the liberation of free radicals from the ternary complex, is at variance with the finding of Hughes and Nicklin[10] that reaction (*F*) is catalysed by free metallic ions, and does not occur in the presence of EDTA. A more detailed study of the catalytic effect of cations on the autooxidation rate of hydroxylamine also showed that this effect cannot be explained only by acceleration of the postulated reaction[11] (*F*). With the aid of isotopically labelled oxygen it would be possible to decide between the two mechanisms with certainty. If the reaction proceeds *via* peroxonitrite, at least one oxygen atom in the formed nitrite must come from molecular oxygen. If nitrite is formed by a four-electron transfer within the complex, one of its oxygen atoms must come from water.

In the autooxidation of hydrazine it is more difficult to identify the products of the individual reactions since most of them lead to the formation of nitrogen. In contrast to what was expected the reaction mixture contained hydrogen peroxide, whose relative concentration, $[H_2O_2]/\Delta O_2$, increased during the reaction up to 100% (Fig. 3). This demonstrates that not only the 4-electron oxidation of hydrazine is not a preferential reaction, but can be fully suppressed.

The assumption that after the transfer of 1 or 2 electrons the ternary complex liberates radicals $N_2H_3^{\bullet}$ and $N_2H_2^{\bullet\bullet}$ would account for the formation of hydrogen peroxide. However, dimerization of the radicals would also have to give rise to ammonia as a final product[12], but only traces of it were found in the reaction mixture.

If the whole oxidation proceeds within the coordination sphere the formation of hydrogen peroxide can be ascribed to oxygen displacing hydrogen peroxide from the ternary complex, so that the oxidation is a two- step process:

$$\begin{gathered} O_2.CoTSP.N_2H_4 \longrightarrow H_2O_2.CoTSP.N_2H_2 \xrightarrow{O_2} \\ \longrightarrow O_2.CoTSP.N_2H_2 \longrightarrow H_2O_2 + CoTSP + N_2\,. \end{gathered} \tag{H}$$

Equation (*3*) shows that a similar displacement cannot occur in the case of hydroxylamine, but the difference in nature of the substrate may have some effect. The fact that the relative concentration of hydrogen peroxide increased with the concentration of CoTSP (Fig. 3) can be expressed by a modification of mechanism (*H*), assuming bridge bonding of hydrazine to CoTSP:

$$\begin{gathered} O_2.CoTSP.N_2H_4.CoTSP \longrightarrow H_2O_2.CoTSP.N_2H_2.CoTSP \xrightarrow{O_2} \\ \longrightarrow H_2O_2.CoTSP.N_2H_2.CoTSP.O_2 \longrightarrow 2\,H_2O_2 + 2\,CoTSP + N_2\,. \end{gathered} \tag{I}$$

Complexes with bonds of this type have been described. They are known to form polymeric chains[13], which is not at variance with the fact that only a complex CoTSP : N_2H_4 ≐ 1 : 1 was found[1] in an anaerobic medium. Despite these obscure points the non-radical mechanism seems to be a more probable one, especially because it does not include the formation of a new N–N linkage.

What the autooxidations of hydroxylamine and hydrazine have in common is the formation of a ternary complex with CoTSP in the first step of the reaction. In all probability the whole oxidation process occurs within this complex. Nevertheless, the two reactions differ in the detailed mechanism of electron transfer, particularly in facility of the 4-electron transfer. The main cause of the difference seems to be the N–N bond in hydrazine and the fact that hydrazine, unlike hydroxylamine, is a bidentate ligand.

REFERENCES

1. Wagnerová D. M., Schwertnerová E., Vepřek-Šiška J.: This Journal *38*, 756 (1973).
2. Weber J. H., Busch D. H.: Inorg. Chem. *4*, 469 (1965).
3. Laidler K. J.: *The Chemical Kinetics of Enzyme Action.* Clarendon Press, p. 73. Oxford 1973.
4. Wagnerová D. M., Schwertnerová E., Vepřek-Šiška J.: This Journal *39*, 1980 (1974).
5. Waldmeier P., Sigel H.: Chimia (Aarau) *24*, 195 (1970).

6. Sigel H.: Chimia (Aarau) *21*, 490 (1967).
7. Huber P. R., Griesser R., Prijs B., Sigel H.: Eur. J. Biochem. *10*, 238 (1969).
8. Griesser R., Sigel H.: Inorg. Chem. *10*, 2229 (1971).
9. Bayer E., Schretzmann O.: Structure and Bonding *2*, 181 (1967).
10. Hughes M. N., Nicklin H. G.: J. Chem. Soc. A *165* (1971).
11. Luňák S.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1972.
12. Higginson W. C. E., Weight P.: J. Chem. Soc. *1551*, (1955).
13. Bottomley F.: Quart. Rev. *24*, 617 (1970).

Translated by J. Salák.