Catalytic effect of $Cu(TAAB)^{2+}$ on ascorbic acid dioxygen oxidation

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Polarographic and spectrophotometric study has been made of the kinetics of ascorbic acid dioxygen oxidation catalyzed by copper complex with a tetrabenzo(b,f,j,n)(1,5,9,13)tetraazacyclohexadecine (TAAB) macrocyclic ligand. A chain radical mechanism has been suggested assuming $Cu(TAAB)^{2+}$ reduction by ascorbic acid to be a rate-determining step and a fast $Cu(TAAB)^{+}$ reoxidation process.

Полярографическим и спектрофотометрическим методами изучена кинетика окисления аскорбиновой кислоты молекулярным кислородом, катализируемого комплексом меди с макроциклическим лигандом тетрабензо(b,f,j,n)(1,5,9,13)тетраазациклогексадецином (TAAB). Предложен цепной механизм с участием радикалов предполагающий восстановление $Cu(TAAB)^{2+}$ аскорбиновой кислотой скорость определяющей стадией и быстрое последовательное окисление $Cu(TAAB)^{+}$

Some copper complexes with macrocyclic ligands have led to further investigation into dioxygen and superoxide ion reactions [1, 2]. From this point of view it is interesting to examine the catalytic activity of such complexes in reactions of an oxidase type.

In such cases, for copper ions and its complexes the most often studied oxidation is that of the ascorbic acid for reasons of its biological and biochemical importance. Results obtained so far are summarized and critically assessed in papers [3, 4].

The present paper treats of the reactivity of copper complex with tetrabenzo(b,f,j,n)(1,5,9,13)tetraazacyclohexadecine, commonly indicated as $Cu(TAAB)^{2+}$. Its catalytic properties have been determined in a previous study [5].

Experimental

Ascorbic acid — H_2Asc (Spofa, Prague): Solutions were prepared immediately before the experiments directly from the weighed-out material. $Cu(TAAB)(NO_3)_2$ was synthesized as indicated in paper [6]. Britton—Robinson buffer solutions were prepared from anal. grade chemicals in redistilled water, the ionic strength being adjusted with KNO_3 ($I = 0.1$ mol dm^{-3}). H_2O_2 was of anal. grade (Lachema, Brno). The concentration of stock H_2O_2 solutions was iodometrically determined and so was the O_2 concentration given by air solubility [7, 8]. Inert gas employed was incandescent lamp nitrogen.

The polarization curves of reactants were voltammetrically monitored. Changes in dioxygen and H_2O_2 concentration in the course of the catalyzed reaction were polarographically monitored at -0.45 V (O_2) and -1.1 V (H_2O_2) potentials, respectively. The polarograph used was the OH-102 type (Radelkis, Budapest). The indicating electrode employed was a platinum microelectrode and a dropping mercury electrode (DME) ($t_1 = 5.4$ s, $m_r = 7.7 \times 10^{-4}$ g s^{-1}, $h = 53$ cm), the reference electrode was a saturated calomel electrode (SCE) and all potentials in this paper are referred to this electrode. The airtight polarographic cell was adjusted so as to be bubbled through by inert gas or compressed air.

The reduction of Cu complex was spectrophotometrically monitored at the $Cu(TAAB)^+$ maximum absorption wavelength ($\lambda = 660$ nm, $\varepsilon = 5200$ cm^{-1} mol^{-1} dm^3 [5]), at which $Cu(TAAB)^{2+}$ absorption is negligible. Use was made of the Specol spectrophotometer (Zeiss, Jena) with a recorder of the type G1B1 (Zeiss, Jena) and of the UV VIS Specord (Zeiss, Jena). Measuring cells of the D 5 cm Kleinküvette type (GFR) were closed but provided with filling and bubble aeration holes. All the solutions were of constant temperature of 25.0 °C. Measurements of pH were made with a pH-meter, Type OP-201/2 (Radelkis, Budapest).

Kinetic parameters were calculated by linear regression.

Results

Binary interactions

Our study of reducing $Cu(TAAB)^{2+}$ to $Cu(TAAB)^+$ using ascorbic acid in anaerobic conditions has been based on results contained in paper [9].

The typical course of the increase in concentration of the complex reduced form in dependence on time corresponds to curve *a* in Fig. 1. The reaction is of the pseudofirst order with respect to Cu complex, which has been verified for three different $Cu(TAAB)^{2+}$ initial concentrations. It is characterized by observed rate constant $k_{obs,Cu}$, which corresponds, with regard to stoichiometry [9], to one half of the slope of linear dependence ln $(A_\infty - A)$ *vs.* time, where A is the absorbance of the complex reduced form.

Observed rate constant $k_{obs,Cu}$ rises with the icreasing ascorbic acid concentration (c_A) and tends towards its limit value (Fig. 2*a*). Its trend is evidence of ascorbic acid

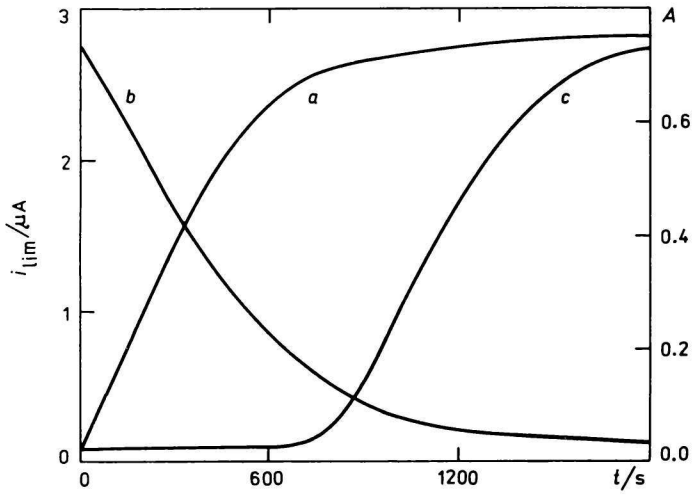

Fig. 1. Time concentration profiles of $Cu(TAAB)^+$ and O_2.
a) Absorbance time dependence of the reduced form of complex, *i.e.* $Cu(TAAB)^+$ ($\lambda = 660$ nm, $\varepsilon = 5200$ cm^{-1} mol^{-1} dm^3, $l = 5$ cm), anaerobic conditions; *b*) time dependence of the limiting diffusion current of the O_2 first-step reduction on a DME at $E = -0.45$ V *vs.* SCE; *c*) as under *a*) but in the presence of O_2.
Britton—Robinson buffer solution, pH = 3.5, ionic strength $I = 0.1$ mol dm^{-3}, initial concentrations: c(ascorbic acid) $= 3 \times 10^{-3}$ mol dm^{-3}, $c(Cu(TAAB)^{2+}) = 3 \times 10^{-5}$ mol dm^{-3}, $c(O_2) = 2.6 \times 10^{-4}$ mol dm^{-3}, $t = 25$ °C.

saturation and may be expressed by the following relation

$$k_{obs,Cu} = \frac{k_1 K_1 c_A}{1 + K_1 c_A} \qquad (1)$$

where rate constant $k_1 = 4.1 \times 10^{-3}$ s^{-1} (for pH = 3.45) and equilibrium constant $K_1 = 353$ mol^{-1} dm^3. Dependence $k_{obs,Cu}$ on activity H^+ takes the form

$$k_{obs,Cu} = k_2 \frac{1}{a_{H^+}} \qquad (2)$$

where $k_2 = 8.5 \times 10^{-7}$ s^{-1} mol dm^{-3} for $c_A = 3 \times 10^{-3}$ mol dm^{-3}. Comparing eqns (*1*) and (*2*) we get

$$k_{obs,Cu} = \frac{k K_1 c_A}{1 + K_1 c_A} \cdot \frac{1}{a_{H^+}} \qquad (3)$$

where rate constant $k = 1.5 \times 10^{-6}$ s^{-1} mol dm^{-3}.

As ionic strength I is increasing from 0.05 to 1.00 mol dm^{-3} the value of $k_{obs,Cu}$ decreases. From linear dependence log $\{k_{obs,Cu}\}$ *vs.* $\sqrt{I}/(1 + 1.4\sqrt{I})$ and from the

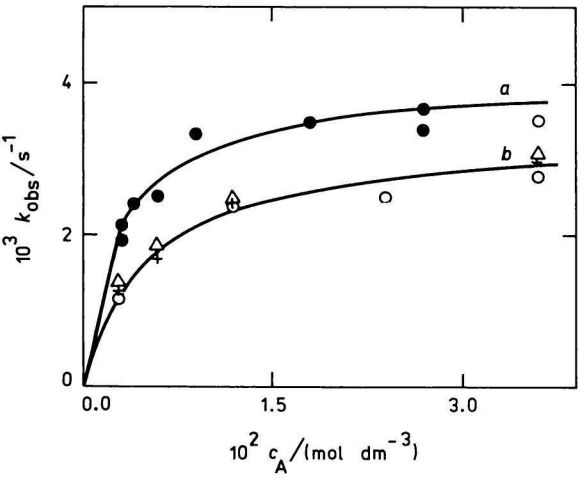

Fig. 2. Effect of ascorbic acid concentration (c_A) on observed rate constants.
a) Dependence of $k_{obs,Cu}$ on c_A in anaerobic conditions, pH = 3.45; *b*) dependence of $k_{obs,D}$ on c_A in a catalyzed system, pH = 2.85, initial O_2 concentration: + $c(O_2) = 2.6 \times 10^{-4}$ mol dm^{-3}, Δ $c(O_2) = 1.8 \times 10^{-4}$ mol dm^{-3}, ○ $c(O_2) = 8.3 \times 10^{-5}$ mol dm^{-3}
Britton—Robinson buffer solution, ionic strength $I = 0.1$ mol dm^{-3}, initial concentration $c(Cu(TAAB)^{2+}) = 3 \times 10^{-5}$ mol dm^{-3}, $t = 25$ °C.
The course of curves was calculated using eqns (*1*) and (*4*).

corresponding line slope value (−2.1) it follows that a reaction of particles of opposite charge takes place.

The interaction of $Cu(TAAB)^{2+}$ with O_2 as well as with H_2O_2 was examined spectrophotometrically in the region of 450—700 nm wavelengths, where values of ε were not excessive. No difference was observed between the $Cu(TAAB)^{2+}$ ($c_{Cu} = 3 \times 10^{-5}$ mol dm^{-3}) spectrum recorded with O_2 present and that taken after removing O_2 or after the solution had been reaerated. Nor was any change noticeable in the $Cu(TAAB)^{2+}$ spectrum recorded in the H_2O_2 solution ($c_P = 9 \times \times 10^{-3}$ mol dm^{-3}).

$Cu(TAAB)^{+}$ complex could not be spectrophotometrically examined because of its limited solubility (formation of precipitates). It was studied voltammetrically on a stationary platinum microelectrode in dimethyl sulfoxide. $Cu(TAAB)^{2+}$ electrochemical reduction (peak potential $E_p = -0.08$ V) is quasi-reversible and after the change of polarization direction a $Cu(TAAB)^{+}$ anodic peak may be observed ($E_p = 0.02$ V). The dioxygen reduction to superoxide $\cdot O_2^-$ [2], in the absence of Cu complex, is also quasi-reversible in this solvent (cathodic peak $E_p = -1.00$ V, anodic counterpeak $E_p = -0.75$ V). No $\cdot O_2^-$ and $Cu(TAAB)^{+}$ anodic peaks, however, were observed after the O_2 reduction in the presence of $Cu(TAAB)^{2+}$ (or if any, then they were very small if a high polarization scan rate was used) which is evidence of $\cdot O_2^-$ and $Cu(TAAB)^{+}$ chemical interaction.

No decrease in the O_2 concentration was recorded in the ascorbic acid solution ($c_A = 3 \times 10^{-3}$ mol dm^{-3}) within the range of pH from 2.85 to 4.00, if there was no Cu catalyst present. At higher pH values (5—7), however, there was a marked consumption of O_2. The reaction of H_2O_2 ($c_P = 1.2 \times 10^{-3}$ mol dm^{-3}) with the ascorbic acid ($c_A = 3 \times 10^{-3}$ mol dm^{-3}) in the absence of the catalyst in pH = = 2.85—4.00 is also very slow.

Ascorbic acid dioxygen oxidation in the presence of $Cu(TAAB)^{2+}$

Fig. 1*b* shows typical changes in the O_2 concentration in the course of the reaction. At the beginning of the O_2 reaction there was a short induction period. The reaction rate was assessed after this induction period as in the case of a pseudofirst-order reaction with respect to O_2. Observed rate constant $k_{obs,D}$ was calculated as the $\ln \{i_{lim,D} - i_{lim_\infty,D}\}$ dependence *vs.* time slope, where i_{lim} is the limiting diffusion current of the first step of O_2 reduction, the linearity of this dependence being characterized by its correlation coefficient values of -0.990 to -0.999.

A separate examination of the ascorbic acid anodic wave limiting current has confirmed that under reaction conditions studied there is, simultaneously with the decrease in the O_2 concentration, a drop in that of the ascorbic acid. The presence of H_2O_2 as a product of O_2 reduction has been polarographically verified and so was its slow further reaction until it has been completely used up.

Observed dioxygen decrease rate constant $k_{obs,D}$ is a function of the ascorbic acid concentration (Fig. 2*b*). The dependence was identical for three different initial O_2 concentrations and may be expressed as

$$k_{obs,D} = \frac{k_{1,D} K_{1,D} c_A}{1 + K_{1,D} c_A} \qquad (4)$$

where $k_{1,D} = 3.4 \times 10^{-3}$ s^{-1} (for pH = 2.85 and $c_{Cu} = 3 \times 10^{-5}$ mol dm^{-3}) and $K_{1,D} =$ $= 180$ mol^{-1} dm^3. Value $k_{obs,D}$ rises with increasing pH of the solution, and it holds that

$$k_{obs,D} = k_{2,D} \frac{1}{a_{H^+}} \qquad (5)$$

where $k_{2,D} = 7.7 \times 10^{-7}$ mol dm^{-3} s^{-1} for $c_A = 3 \times 10^{-3}$ mol dm^{-3} and $c_{Cu} =$ $= 3 \times 10^{-5}$ mol dm^{-3} Comparing this with eqn (*4*) we get rate law

$$k_{obs,D} = \frac{k_{3,D} K_{1,D} c_A}{1 + K_{1,D} c_A} \cdot \frac{1}{a_{H^+}} \qquad (6)$$

where $k_{3,D} = (2.2 \text{ to } 4.6) \times 10^{-6}$ s^{-1} mol dm^{-3} for $c_{Cu} = 3 \times 10^{-5}$ mol dm^{-3}.

If the value of a_{H^+} is known, ascorbic acid concentration (c_A) may be expressed in terms of concentration of a once-deprotonized $HAsc^-$ form. Such a reduction was

done for all the experimental points of the two described dependences: $k_{obs,D}$ *vs.* c_A (pH = 2.85) and $k_{obs,D}$ *vs.* $1/a_{H^+}$ ($c_A = 3 \times 10^{-3}$ mol dm^{-3}) and values $k_{obs,D}$ were plotted against those of equilibrium $HAsc^-$ concentration. Two new mutually diverse dependences were thus obtained. At an equal $HAsc^-$ concentration, $k_{obs,D}$ is markedly greater at higher pH values. Coefficient $1/a_{H^+}$ in the kinetic equation does not, therefore, represent ascorbic acid dissociation (or if it does, then to a very small extent) but, just as in anaerobic conditions [7], it is connected with the presence of OH^- ions in the chemical reaction.

The effect of $Cu(TAAB)^{2+}$ concentration (c_{Cu}) has also been verified and saturation observed — for $c_{Cu} > 1 \times 10^{-4}$ mol dm^{-3}, $k_{obs,D}$ tends towards its limit value ($k_{obs,D} = 3 \times 10^{-3}$ s^{-1} for pH = 2.85, $c_A = 3 \times 10^{-3}$ mol dm^{-3}, 25 °C).

The dependence of rate constant logarithm $\log \{k_{obs,D}\}$ on the square root of ionic strength I is the same as in the $Cu(TAAB)^{2+}$ reaction with the ascorbic acid in an anaerobic medium.

Fig. 1*c* shows a typical record of the changes in the Cu catalyst spectrophotometrically examined. The diagram proves that a catalyst reduced form is produced in measurable concentration only after a period necessary for the greatest quantity of dioxygen present in the solution to be reacted on. The duration of the Cu complex absorbance initial value is shortened if O_2 is removed from the solution, bubbled through with nitrogen. In the presence of acrylonitrile (10 vol. %) the $Cu(TAAB)^{2+}$ reduction, even in aerobic conditions, corresponds to that represented in Fig. 1*a*, with O_2 consumption at a markedly slow rate. At high ascorbic acid concentrations acrylonitrile polymerizes in this system. The presence of radicals, however, has not been spectrophotometrically revealed, not even with the use of the EPR technique.

Reactions after dioxygen consumption and the effect of H_2O_2

After O_2 had been spent, the $Cu(TAAB)^{2+}$ reduction (in the presence of H_2O_2 resulting from reduction of O_2, Fig. 1*c*) followed a course similar to that in anaerobic conditions (Fig. 1*a*) and could be described as dependence $\ln (A_\infty - A)$ on time. After making allowance for the decrease in ascorbic acid through its reaction with dioxygen, rate constant values amounted to 60—80 % of $k_{obs,Cu}$ in anaerobic conditions.

Efforts at reoxidizing $Cu(TAAB)^+$ in the course of the reduction process by introducing air into the solution still containing an excess of ascorbic acid have not proved successful. All that had been achieved was to slow-down further $Cu(TAAB)^{2+}$ reduction.

In the excess of H_2O_2, in anaerobic conditions, and in the presence of ascorbic acid ($c_A = 3 \times 10^{-3}$ mol dm^{-3}) the $Cu(TAAB)^{2+}$ reduction reaction rate is greater than that in equivalent conditions without H_2O_2. Dependence $k_{obs,Cu}$ on H_2O_2 concentration is shown in Fig. 3*a*. In the absence of ascorbic acid H_2O_2 had no

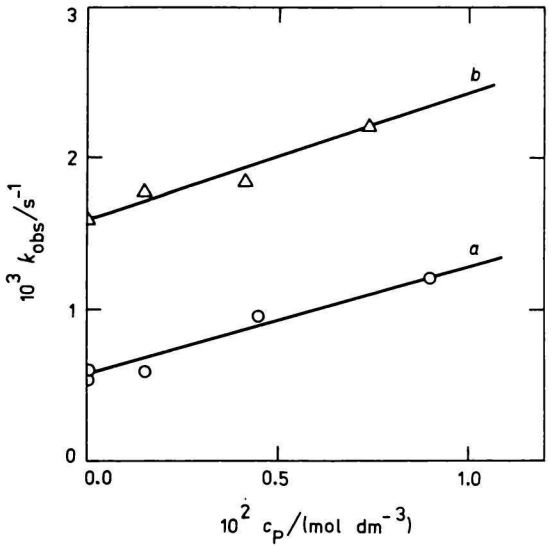

Fig. 3. Effect of H_2O_2 concentration (c_P) on observed rate constants.
a) Dependence of $k_{obs,Cu}$ on c_P in anaerobic conditions; *b*) dependence of $k_{obs,D}$ on c_P in a catalyzed system, initial dioxygen concentration $c(O_2) = 2.6 \times 10^{-4}$ mol dm^{-3}
Britton—Robinson buffer solution, pH = 2.85, ionic strength $I = 0.1$ mol dm^{-3}, initial concentrations: c(ascorbic acid) $= 3 \times 10^{-3}$ mol dm^{-3}, $c(Cu(TAAB)^{2+}) = 3 \times 10^{-5}$ mol dm^{-3}, $t = 25$ °C.

reductive effect on $Cu(TAAB)^{2+}$ H_2O_2, therefore, acts on the Cu(II) complex as a one-electron reductant in case the "draw-off" of its one-electron oxidation product in the system ($\cdot HO_2$ radical reaction with $HAsc^-$) has been ensured. However, the effect of H_2O_2 on $Cu(TAAB)^{2+}$ reduction is only slight in view of the high H_2O_2 concentrations required.

Monitoring the H_2O_2 excess (initial concentrations: $c_P = 1 \times 10^{-3}$ mol dm^{-3}, $c_A = 3 \times 10^{-3}$ mol dm^{-3}, $c_{Cu} = 3 \times 10^{-5}$ mol dm^{-3}; pH = 3.5, O_2 bubbled out beforehand) and quantitatively evaluating dependence $\ln \{i_{lim,P} - i_{lim\infty,P}\}$ *vs.* time, where $i_{lim,P}$ is the limiting diffusion current of H_2O_2, we obtained the value of $k_{obs,P} = 2.8 \times 10^{-4}$ s^{-1}.

The effect of H_2O_2 on the O_2 decrease in a typically catalyzed system ($c_A = 3 \times$ $\times 10^{-3}$ mol dm^{-3}, $c_{Cu} = 3 \times 10^{-5}$ mol dm^{-3}, pH = 2.85, initial O_2 concentration $c(O_2) = 2.6 \times 10^{-4}$ mol dm^{-3}) is illustrated in Fig. 3*b*. It shows the relation between the increased $Cu(TAAB)^+$ formation and dioxygen consumption. An induction period in the O_2 decrease has also been observed in solutions with a high H_2O_2 concentration but was markedly shorter when compared with that under conditions without the addition of H_2O_2.

Discussion

Results obtained from $Cu(TAAB)^{2+}$ reaction with ascorbic acid have confirmed the authors' findings in paper [9]. Experiments with high ascorbic acid concentrations (c_A) have further provided kinetic evidence of prearranged complexing equilibrium and have enabled us to determine the value of the reaction rate and equilibrium constants. Value $K = 353$ mol^{-1} dm^3 is proof of a pretty considerable bonding strength of the ascorbic acid anion.

For the mechanism of the ascorbic acid catalyzed oxidation three ways of electron exchange between ascorbic acid and dioxygen may, in principle, be considered:

a) the ternary complex of the O_2—Cu—$HAsc^+$ or O_2—CuL—$HAsc^+$ type,
b) chain mechanism,
c) coordination-bonded ascorbic acid outer-sphere oxidation.

Ternary complex formation was considered in the catalysis by cupric chelates either after the Cu(II) reduction to Cu(I) and after the chelate-forming ligand dissociation [7, 10] or even for the Cu(II)L complex [11, 12]. Such a mechanism has also been proposed for the copper-macrocyclic complex catalysis, the complex being irreducible by ascorbic acid, and the induction period observed in the O_2 decrease has been understood to be the time needed for the ternary complex formation [13]. In our case there are several facts that go against this view: The bond of the TAAB ligand is too strong both for $Cu(TAAB)^{2+}$ and $Cu(TAAB)^+$ to make any reaction of a dissociated copper ion worth considering; dioxygen is rarely bonded with a Cu-macrocyclic complex [1, 2]; excessive electron delocalization of the TAAB ligand will hardly make simultaneous coordination of $HAsc^-$ and O_2 possible [14].

$Cu(TAAB)^{2+}$ reduction in an anaerobic medium has a few features in common with dioxygen reduction, *viz.* the same form of kinetic equation; same dependence $\log \{k_{obs}\}$ *vs.* $\sqrt{I}$, where I is the solution ionic strength; similar effect on both by the addition of H_2O_2.

Another significant fact is that during the O_2 reduction (up to a marked drop in O_2 concentration) the reaction system shows absorbance identical with that of $Cu(TAAB)^{2+}$ in the initial concentration (Fig. 1*c*) and that in the presence of acrylonitrile serving as an interceptor of radicals there is an immediate increase in the $Cu(TAAB)^+$ concentration at an equal rate with that in anaerobic conditions, the rate of O_2 decrease being essentially lower. All this leads to the view that $Cu(TAAB)^+$ formation is a rate-determining step in the ascorbic acid catalyzed oxidation and that $Cu(TAAB)^+$ reoxidation proceeds very fast. Since $Cu(TAAB)^+$ is not directly oxidizable by dioxygen (and if at all, then only very slowly) it must be its more reactive form that participates in the reoxidation and this may be $\cdot HO_2$ as was confirmed by voltammetric measurements. Cu(I) reoxidation has already been

dealt with in connection with another chelate [15], in which dioxygen was reduced by the exchange of four electrons all the way to water.

The proposed chain radical mechanism may be expressed by the following reactions

$$H_2Asc \rightleftarrows HAsc^- + H^+ \qquad (A)$$

$$Cu(TAAB)^{2+} + HAsc^- \rightleftarrows Cu(TAAB)(HAsc)^+ \qquad (B)$$

$$Cu(TAAB)(HAsc)^+ \rightarrow Cu(TAAB)^+ + \cdot Asc^- + H^+ \qquad (C)$$

$$\cdot Asc^- + O_2 + H^+ \rightarrow DAsc + \cdot HO_2 \qquad (D)$$

$$\cdot HO_2 + Cu(TAAB)^+ \rightarrow HO_2^- + Cu(TAAB)^{2+} \qquad (E)$$

where DAsc indicates dehydroascorbic acid. Reactions (D) and (E) are sufficiently fast in comparison with reaction (C) and do not proceed only when there is a marked decrease in O_2. The above reaction scheme has been simplified; other forms of ascorbic acid may also react [16] and further reactions do also take place

$$\cdot HO_2 + HAsc^- \rightarrow HO_2^- + \cdot Asc^- + H^+ \qquad (F)$$

$$\cdot HO_2 + \cdot Asc^- \rightarrow HO_2^- + DAsc \qquad (G)$$

$$Cu(TAAB)^{2+} + \cdot Asc^- \rightarrow Cu(TAAB)^+ + DAsc \qquad (H)$$

and the disproportionation of $\cdot Asc^-$ and $\cdot HO_2$ [17].

The existence of an induction period at the decreasing of O_2 (in Fig. 1*b* it can be but slightly observed owing to the generally high reaction rate) is probably connected with the formation of a certain degree of $\cdot Asc^-$ concentration, which afterwards lasts as long as the $Cu(TAAB)^{2+}$ concentration remains constant. According to [18] such an induction period is not a rare phenomenon in oxidations catalyzed by copper complexes with N-donor ligands and is connected with the formation of a sufficiently great amount of a joint catalyst or "promoter"

$Cu(TAAB)^{2+}$ complex, when compared with either complexes [3, 4] under study or even with a copper-containing enzyme (ascorbateoxidase) [19], in many respects represents a special type of catalyst. Its catalytic effect is not less than that of Cu^{2+} aquo ion ($CuSO_4$); it leads to a partial reduction of O_2, retains the form of Cu(II) complex so long as O_2 remains in the solution and raises the reduction rate of O_2 on H_2O_2 addition. The reaction thus resembles the catalysis by synthetic porphyrin complexes [20].

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