

Effect of fumarate on the kinetics and reaction mechanism of Cu^+_{aq} with dioxygen

Nadav Navon,^a Haim Cohen,^{ab} Rudi van Eldik^c and Dan Meyerstein^{ad}

^a Chemistry Department, Ben-Gurion University of the Negev, Beer-Sheva, Israel

^b Nuclear Research Centre Negev, Beer-Sheva, Israel

^c Institute for Inorganic Chemistry, University of Erlangen-Nuernberg, 91058 Erlangen, Germany

^d The College of Judea and Samaria, Ariel, Israel

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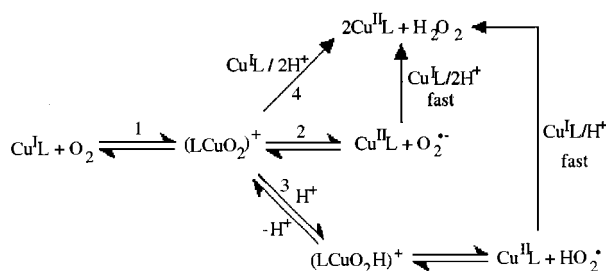
The kinetics of the reactions: $\text{Cu}^+_{\text{aq}} + \text{O}_2 \rightleftharpoons (\text{CuO}_2)^+_{\text{aq}}$ and $(\text{CuO}_2)^+ + \text{Cu}^+_{\text{aq}} \xrightarrow{\text{H}^+} 2\text{Cu}^{2+}_{\text{aq}} + \text{H}_2\text{O}_2$ were studied applying the pulse radiolysis technique, $Kk = (2.3 \pm 0.4) \times 10^8 \text{ dm}^6 \text{ s}^{-1} \text{ mol}^{-2}$, in good agreement with the value calculated from literature data. The complex $\text{Cu}^{\text{I}}(\text{fum})$ (fum = fumarate) reacts considerably slower than Cu^+_{aq} with dioxygen so that the rate law reflects only the reaction of Cu^+_{aq} . A comparison of the results with those reported for the ligands L (water, CH_3CN , phenanthroline, bipyridine or fumarate) indicates that the ligand affects the stability constant of the $\text{Cu}^{\text{I}}\text{L}\cdot\text{O}_2$ complex, and for fumarate also the subsequent reaction.

Introduction

Copper(I) complexes are catalysts for a large variety of processes.¹⁻³ Therefore it is of interest to study the effect of ligands on the kinetics and mechanisms of Cu(I) complexes. The reactions of copper(I) complexes with dioxygen are of special importance due to their role in biological and catalytic systems including oxidation processes by dioxygen and peroxides.⁴ Copper(I) complexes with alkenes are abundant. It seemed therefore of interest to study the effect of an alkene, fumarate, on the reaction between Cu^+_{aq} and dioxygen.

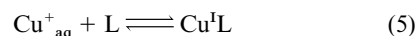
In principle ligands affect the reactivity of Cu(I) due to one of the following reasons. (1) If the stability constants of the Cu(I) complexes with the ligand are larger than those of the corresponding Cu(II) complexes then the redox potential of the $\text{Cu}^{\text{III}}/\text{Cu}^{\text{I}}$ couple is shifted anodically, *i.e.* the Cu(I) complex is a weaker reducing agent than Cu^+_{aq} , and *vice versa*. (2) Ligands can slow down the rate of Cu(I) reactions due to steric effects.

The reaction mechanisms of several Cu(I) complexes with dioxygen were studied.⁴⁻⁸ The experimental evidence shows that $\text{LCu}^{\text{I}}\text{O}_2$ complexes are formed as key intermediates in the mechanism. The conclusion that $\text{LCu}^{\text{I}}\text{O}_2$ complexes are formed is based on kinetic arguments in each system. However using the Marcus cross relation⁹ it can be shown that the reaction is always considerably faster than that calculated from the redox potentials and the self exchange rate of $\text{Cu}^{\text{III}}\text{L}$ and $\text{O}_2/\text{O}_2^{\cdot-}$. Thus for example the redox potentials for $\text{Cu}^{\text{III}}_{\text{aq}}$ and $\text{O}_2/\text{O}_2^{\cdot-}$ are 0.15 V and -0.33 V respectively, the rate of the self exchange reaction of Cu^+_{aq} and $\text{Cu}^{2+}_{\text{aq}}$ is $5 \times 10^{-7} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ¹⁰ and that of O_2 and $\text{O}_2^{\cdot-}$ is $450 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.¹¹ Using these values one calculates that the rate of the reaction $\text{Cu}^+_{\text{aq}} + \text{O}_2 \rightarrow \text{Cu}^{2+}_{\text{aq}} + \text{O}_2^{\cdot-}$ should be $1.6 \times 10^{-6} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ whereas the observed rate is $3.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.^{5,6b} Thus $\text{LCu}^{\text{I}}\text{O}_2$ has to be an intermediate in all systems. Therefore schematically the reaction mechanism of $\text{Cu}^{\text{I}}\text{L}$ with O_2 is described in Scheme 1.⁵ According to this scheme the observed rate law in the presence of excess dioxygen is expected to consist of two parts. (1) First order in $[\text{Cu}^{\text{I}}\text{L}]$ due to the contribution of reactions (2) and (3) in the absence of excess $\text{Cu}^{\text{II}}\text{L}$. (2) Second order in $[\text{Cu}^{\text{I}}\text{L}]$ due to the contribution of reaction (4), or to reactions (2) and (3) in the presence of excess $\text{Cu}^{\text{II}}\text{L}$. In the latter case the rate is inversely proportional to $[\text{Cu}^{2+}_{\text{aq}}]$. This



Scheme 1

scheme is complicated by the equilibrium (5) (it is assumed



that no $\text{Cu}^{\text{I}}\text{L}_2$ complexes are formed as these are rare for alkenes) as the ligands L clearly affect the different rates and equilibrium constants of the reactions in Scheme 1. For ligands which slow down the reaction of Cu(I) with O_2 , alkenes are such ligands,⁸ the dependence of the observed rate of reaction on $[\text{L}]$ is expected to obey, in the extreme cases, one of the following laws. (1) The rate of the reaction will be independent of $[\text{L}]$ if the stability constant of $\text{Cu}^{\text{I}}\text{L}$ is so high that the steady state concentration of Cu^+_{aq} is so low that all the reaction proceeds *via* $\text{Cu}^{\text{I}}\text{L}$. This, for example, is the situation for $\text{L} = \text{phenanthroline}$.³ (2) The rate of the reaction will depend linearly on $[\text{L}]^{-1}$ if: (a) the reaction proceeds only *via* reactions (2) and (3) in Scheme 1 and if only Cu^+_{aq} is reactive. (b) The reaction proceeds *via* reaction (4) in Scheme 1 and Cu^+_{aq} is the sole participant in reaction (1) or (4) and $\text{Cu}^{\text{I}}\text{L}$ is the sole participant in the second reaction. (3) The rate of the reaction will depend linearly on $[\text{L}]^{-2}$ if the reaction proceeds *via* reaction (4) and only Cu^+_{aq} participates. Naturally intermediate dependences on $[\text{L}]$ might be observed if none of these extreme conditions is met. This analysis explains the different dependences on $[\text{L}]$ reported by different investigators.⁵⁻⁸

Alkenes were shown to slow down reactions (2) and/or (3).⁸ However the effect of alkenes on reaction (4) has not been studied. It was therefore decided to study the effect of fumaric acid on the rate of reaction of Cu^+_{aq} with O_2 . For this purpose

solutions containing a large excess of $\text{Cu}^{2+}_{\text{aq}}$, in order to block reactions (2) and (3) were used. Furthermore it was decided to measure the volume of activation of reaction (4) in order to obtain further mechanistic insight. The choice of fumaric acid is due to the strong absorption band of the $d \rightarrow \pi$ $\text{Cu}(\text{I})$ -fumarate complex which facilitates the kinetic measurements.

Experimental

Materials

All solutions were prepared from A.R. grade chemicals and from distilled water further purified by passing through a Milli Q Millipore setup, final resistivity $>10 \text{ M}\Omega \text{ cm}^{-1}$. The pH was measured with a Corning 220 pH meter, and was adjusted by HClO_4 and/or NaOH . Solutions containing different concentrations of O_2 were prepared by mixing, in different ratios, two identical solutions one of which was N_2O saturated and the other was O_2 saturated using the syringe technique.

Pulse-radiolysis experiments

These were carried out using the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem. The pulse duration was 0.1–1.5 μs with a 200 mA current of 5 MeV electrons. The dose per pulse was 300–3000 rads. Irradiations were carried out in a 4 cm Spectrosil optical cell the analyzing light passing three times through the cell. A 150 W xenon arc produced the analyzing light. The experimental setup was identical with the described earlier in detail.^{12,13}

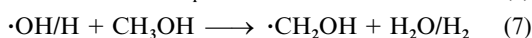
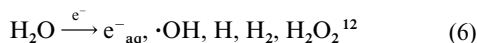
For dosimetry, an N_2O -saturated solution containing $1 \times 10^{-3} \text{ mol dm}^{-3}$ KSCN was used. The yield of $(\text{SCN})_2^{\cdot-}$ was measured by taking $\epsilon_{475} = 7600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and the dose per pulse was calculated assuming $G(\text{SCN})_2^{\cdot-} = 6.0$ ¹² and an optical path of 12.3 cm.

High pressure measurements

These were carried out using the Varian 7715 linear electron accelerator of the Hebrew University of Jerusalem, the experimental setup was identical with that described earlier in detail.¹⁴

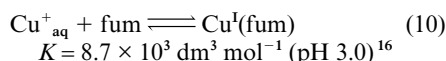
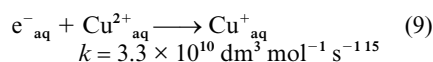
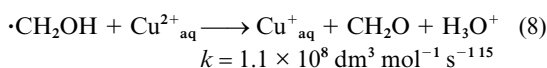
Results and discussion

0–100% N_2O saturated solutions containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , 1 mol dm^{-3} CH_3OH , $0.5\text{--}7 \times 10^{-4} \text{ mol dm}^{-3}$ fumaric acid, $0.1\text{--}1.3 \times 10^{-3} \text{ mol dm}^{-3}$ O_2 at pH 3.0 were irradiated. In these solutions the reactions (6)–(10) (fum = fumarate) have to



$$k_{\text{OH}} = 4.6 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.15}$$

$$k_{\text{H}} = 1.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1.15}$$



be considered. Due to the relatively high concentrations of CuSO_4 and CH_3OH all the primary radicals are converted into $\text{Cu}^{+}_{\text{aq}}$ within less than 2 μs , $[\text{Cu}^{+}_{\text{aq}}]_0 = 2 \mu\text{mol dm}^{-3}$.

The formation of the $\text{Cu}^{\text{I}}(\text{fum})$ complex is indeed observed immediately after the pulse at $\lambda = 350 \text{ nm}$, Fig. 1. In the presence of dioxygen the absorbance of $\text{Cu}^{\text{I}}(\text{fum})$ disappears in a reaction which obeys a second order rate law in $[\text{Cu}(\text{I})]$, Fig. 1. The observed rate constant is linearly proportional to $[\text{O}_2]$, Fig.

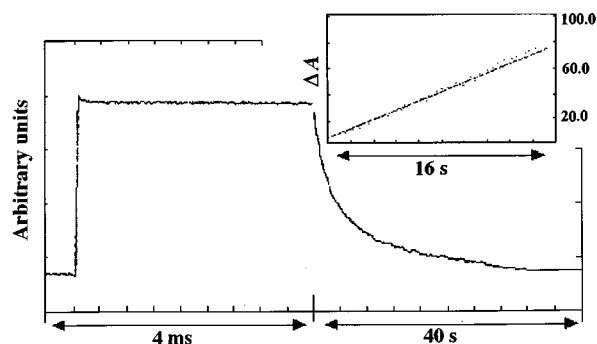


Fig. 1 Computer output of light intensity vs. time. Solution composition: $1.1 \times 10^{-2} \text{ mol dm}^{-3}$ N_2O , $5 \times 10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , 1 mol dm^{-3} CH_3OH , $1 \times 10^{-4} \text{ mol dm}^{-3}$ fumaric acid, $6.5 \times 10^{-4} \text{ mol dm}^{-3}$ O_2 at pH 3.0. Inset: kinetics of the disappearance of the Cu^{I} -fumarate complex, a fit to a second order rate law.

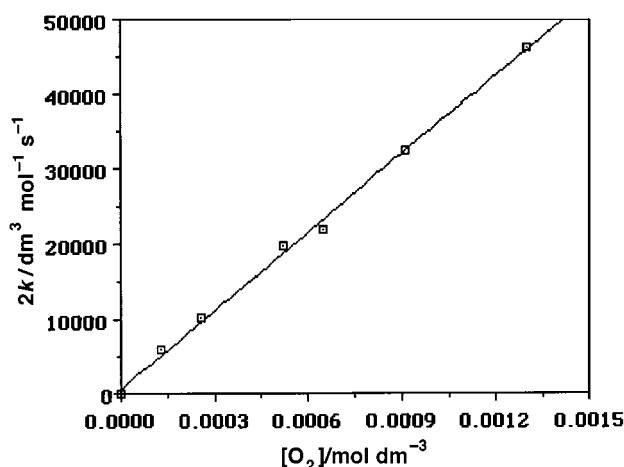


Fig. 2 Dependence of the observed second order rate constant on $[\text{O}_2]$. Solution composition: N_2O saturated, $5 \times 10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , 1 mol dm^{-3} CH_3OH , $2 \times 10^{-4} \text{ mol dm}^{-3}$ fumaric acid at pH 3.0.

2, and depends on the concentration of fumaric acid, Fig. 3. The observed rate is independent of $[\text{Cu}^{2+}_{\text{aq}}]$ in the range $5 \times 10^{-2}\text{--}0.2 \text{ mol dm}^{-3}$. The latter observation shows that indeed reactions (10)–(12) for the oxidation of $\text{Cu}^{+}_{\text{aq}}$ by O_2 seem to fit the experimental results.†



† According to this mechanism the rate law should be:

$$-\frac{d[\text{Cu}^{\text{I}}\text{L}]}{dt} = 2k_{12}[\text{CuO}_2^+][\text{Cu}^{+}_{\text{aq}}] = 2K_{11}k_{12}[\text{O}_2][\text{Cu}^{+}_{\text{aq}}]^2 \quad (\text{I})$$

The total amount of copper(I) is composed of the complexed and the uncomplexed forms of the copper.

$$[\text{Cu}(\text{I})]_{\text{T}} = [\text{Cu}^{\text{I}}\text{L}] + [\text{Cu}^{+}_{\text{aq}}] \quad (\text{II})$$

$$[\text{Cu}^{+}_{\text{aq}}] = \frac{[\text{Cu}(\text{I})]_{\text{T}}}{(K_{10}[\text{L}] + 1)} \quad (\text{III})$$

$$-\frac{d[\text{Cu}^{\text{I}}\text{L}]}{dt} = \frac{2K_{11}k_{12}[\text{O}_2][\text{Cu}(\text{I})]_{\text{T}}^2}{(K_{10})^2[\text{L}]^2 + 2(K_{10})[\text{L}] + 1} \quad (\text{IV})$$

Under the experimental conditions $[\text{O}_2] \gg [\text{Cu}(\text{I})]_{\text{T}}^2$, therefore

$$2k = \frac{K_{11}k_{12}}{(K_{10})^2[\text{L}]^2 + 2(K_{10})[\text{L}] + 1} [\text{O}_2] \quad (\text{V})$$

where k is the observed second order rate constant.

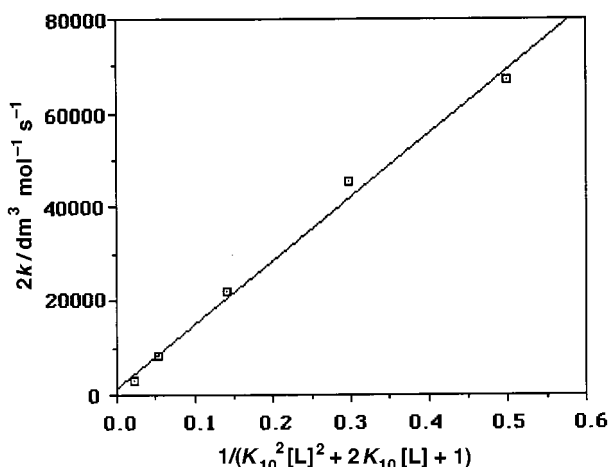
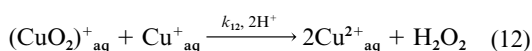
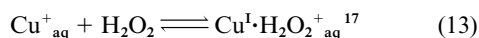


Fig. 3 Dependence of the observed second order rate constant on [fumarate] according to eqn. (V). Solution composition: 1.1×10^{-2} mol dm^{-3} N_2O , 5×10^{-2} mol dm^{-3} CuSO_4 , 1 mol dm^{-3} CH_3OH , 6.5×10^{-4} mol dm^{-3} O_2 at pH 3.

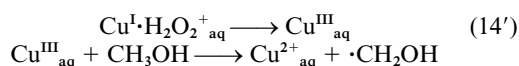
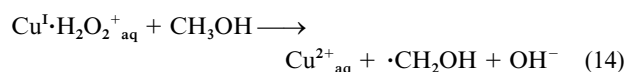


Indeed the results in Fig. 2 show the expected first order dependence of k on $[\text{O}_2]$. Using K_{10} and [fumarate], $K_{11}k_{12} = (2.1 \pm 0.3) \times 10^8 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ is calculated from the slope of Fig. 2. In Fig. 3 the effect of $[\text{L}]$ on $2k$ is plotted according to eqn. (V). The results thus fully corroborate the assumptions used to derive eqn. (V). Furthermore, from the slope of Fig. 3 $K_{11}k_{12} = (2.4 \pm 0.3) \times 10^8 \text{ dm}^6 \text{ s}^{-1} \text{ mol}^{-2}$ is calculated, which is in excellent agreement with the results of Fig. 2. Thus $K_{11}k_{12} = (2.3 \pm 0.4) \times 10^8 \text{ dm}^6 \text{ s}^{-1} \text{ mol}^{-2}$ is derived from the experimental results. The results are in good agreement with $K_{11}k_{12} = 2.8 \times 10^8 \text{ dm}^6 \text{ s}^{-1} \text{ mol}^{-2}$ calculated from ref. 6(c).[‡]

It should be noted that even if reaction (13) is fast, under the



experimental conditions it will not affect the observed rate as it will be followed by eqn. (14) or (14')¹⁷ and then by reaction (8). Thus reaction (13) does not affect $[\text{Cu}^{\text{I}}\text{L}]$.



The results thus point out that the formation of the $d \rightarrow \pi$ complex between Cu(I) and fumarate decreases both K_{11} and k_{12} to a degree that only the reactions of Cu_{aq}^+ are observed under our experimental conditions. This effect is tentatively attributed to the anodic shift of ≈ 220 mV in the redox potential of the $\text{Cu}^{\text{III}}/\text{Cu}^{\text{I}}$ couple upon complexation to the fumarate at pH 3.0.¹⁶

From the observation that there is no deviation from a straight line in Fig. 2 up to $[\text{O}_2] = 1.3 \times 10^{-3} \text{ mol dm}^{-3}$ and that the reaction remains a second order process one calculates $K_{11} < 1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and therefore $k_{12} > 2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The small value of K_{11} suggests that the copper in $\text{CuO}_2^+_{\text{aq}}$ has mainly a Cu(I) nature.

The apparent volume of activation was determined by measuring the effect of pressure, up to 150 MPa, on the observed rate. Solutions containing $5 \times 10^{-2} \text{ mol dm}^{-3}$ CuSO_4 , 1 mol dm^{-3} CH_3OH , $1 \times 10^{-4} \text{ mol dm}^{-3}$ fumarate at pH 3.0 and 4.5– $1.3 \times 10^{-3} \text{ mol dm}^{-3}$ O_2 were irradiated. The observed rate con-

stants increase with the pressure. From the results an apparent volume of activation $\Delta V_{\text{app}}^{\ddagger} = -5.1 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$ is calculated. However as K_{10} is expected to be also pressure dependent ΔV_{10}° was determined, $\Delta V_{10}^{\circ} = -4.5 \pm 1.0 \text{ cm}^3 \text{ mol}^{-1}$. Substitution of the values for K_{10} as a function of pressure into eqn. (V), enables the calculation of $K_{11}k_{12}$ as a function of pressure. This results in $\Delta V_{K_{11}k_{12}}^{\ddagger} = -8.9 \pm 1.5 \text{ cm}^3 \text{ mol}^{-1}$.

The observed volume of activation is equal, according to the suggested mechanism, to the sum of the volume of reaction (11) and the volume of activation of reaction (12), $\Delta V_{K_{11}k_{12}}^{\ddagger} = \Delta V_{11}^{\circ} + \Delta V_{k_{12}}^{\ddagger}$. ΔV_{11}° is expected to have a considerable negative volume as the reaction involves both a bond formation and probably a partial electron transfer from the copper to the dioxygen which is expected to cause a decrease in the copper radius and therefore an increase in its solvation sphere. However, as reaction (12) also involves an oxidative addition, $\Delta V_{k_{12}}^{\ddagger}$ is also expected to have a negative value. The results however suggest that $\Delta V_{k_{12}}^{\ddagger}$ has at most a small negative value. This might be due to one of three reasons. (1) The rate of reaction (12) might approach the diffusion controlled limit, as was proposed for the $\text{Cu}(\text{phen})_2^+$ system,¹⁴ and therefore $\Delta V_{k_{12}}^{\ddagger} \approx 0$. (2) It could be argued that one or even two H^+ ions are required for the reaction to proceed and that the partial loss of their solvation spheres compensates partially the large negative $\Delta V_{k_{12}}^{\ddagger}$ of reaction (12). This is not the case since the rate of the reaction is pH independent between pH 2.3 and 4.1. (3) The transition state of reaction (12) might be an early one. The results do not allow differentiation between points (1) and (3). However the observation, see below, that k_{12} for Cu_{aq}^+ and for $\text{Cu}(\text{CH}_3\text{CN})_2^+$ and probably for $\text{Cu}(\text{phen})_2^+$ has the same value supports the notion that reaction (12) is diffusion controlled. The volume of activation of the analogous reaction, $\text{Cu}(\text{phen})_2^+ + \text{O}_2 \rightleftharpoons \text{Cu}(\text{phen})_2\text{O}_2^+$, was estimated to be $-22 \text{ cm}^3 \text{ mol}^{-1}$,¹⁴ i.e. considerably more negative than $\Delta V_{K_{11}k_{12}}^{\ddagger}$ in the present system. The smaller negative volume of reaction (11) for Cu_{aq}^+ than for $\text{Cu}(\text{phen})_2^+$ can be tentatively accounted for in different ways. Firstly, the bulkier coordination sphere of the phen complex may cause a more effective entrance of the dioxygen molecule into the coordination sphere. Secondly, formation of the $\text{Cu}^{\text{I}}(\text{phen})_2\text{O}_2^+$ complex is expected to change the coordination geometry of $\text{Cu}^{\text{I}}(\text{phen})_2^+$, which may be accompanied by a volume collapse, whereas in the case of the aqua complex dioxygen displaces a coordinated water molecule. Thirdly, partial electron transfer to form a $\text{Cu}^{\text{II}}-\text{O}_2^{\cdot-}$ species might cause a more significant volume collapse for the larger phen complex.

It is of interest to note that $K_{11}k_{12}$ has nearly the same value for four of the five systems for which it was measured: $\text{Cu}_{\text{aq}}^+ + \text{O}_2 \rightleftharpoons (\text{CuO}_2)_{\text{aq}}^+$ followed by $(\text{CuO}_2)_{\text{aq}}^+ + \text{Cu}_{\text{aq}}^+ \longrightarrow 2\text{Cu}_{\text{aq}}^{2+} + \text{H}_2\text{O}_2$; $\text{Cu}_{\text{aq}}^+ + \text{O}_2 \rightleftharpoons (\text{CuO}_2)_{\text{aq}}^+$ followed by $(\text{CuO}_2)_{\text{aq}}^+ + \text{Cu}(\text{CH}_3\text{CN})_2^+ \longrightarrow 2\text{Cu}_{\text{aq}}^{2+} + \text{H}_2\text{O}_2 + 2\text{CH}_3\text{CN}$,^{6c} $\text{Cu}(\text{phen})_2^+ + \text{O}_2 \rightleftharpoons (\text{Cu}(\text{phen})_2\text{O}_2)^+$ followed by $(\text{Cu}(\text{phen})_2\text{O}_2)^+ + \text{Cu}(\text{phen})_2^+ \longrightarrow 2\text{Cu}(\text{phen})_2^{2+} + \text{H}_2\text{O}_2$,^{7,14} $\text{Cu}(\text{bipy})_2^+ + \text{O}_2 \rightleftharpoons (\text{Cu}(\text{bipy})_2\text{O}_2)^+$ followed by $(\text{Cu}(\text{bipy})_2\text{O}_2)^+ + \text{Cu}(\text{bipy})_2^+ \longrightarrow 2\text{Cu}(\text{bipy})_2^{2+} + \text{H}_2\text{O}_2$,¹⁸ for which $K_{11}k_{12} = 2.3 \times 10^8$; 2.8×10^8 ; 2.9×10^8 and $\approx 1 \times 10^8 \text{ dm}^6 \text{ s}^{-1} \text{ mol}^{-2}$ respectively. These results show that k_{12} has the same value for Cu_{aq}^+ and $\text{Cu}(\text{CH}_3\text{CN})_2^+$. On the other hand it was proposed that $k_{12} \geq 1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the phen¹⁴ and bipy¹⁸ systems, i.e. they approach the diffusion controlled limit. As it is unreasonable to suggest that k_{12} is slower for Cu_{aq}^+ than for $\text{Cu}(\text{phen})_2^+$ one has to conclude that reaction (12) is diffusion controlled for all these systems. The only system for which k_{12} is considerably slower is that of $\text{Cu}^{\text{I}}(\text{fum})$. This observation is tentatively attributed to the fact that fumarate is the only ligand in which the copper is bound to an alkene and not to an O or N atom which is mainly a σ donor.

The results thus indicate that K_{11} equals $\approx 0.2 \text{ dm}^3 \text{ mol}^{-1}$ for Cu_{aq}^+ , $\text{Cu}(\text{phen})_2^+$ and for $\text{Cu}(\text{bipy})_2^+$ which all have similar redox potentials (thus for the phen ligand $\beta_2 = 15.82$ ¹⁹ and 16.00²⁰ for Cu(I) and Cu(II) respectively). This value of K_{11}

[‡] $K_{11}k_{12}$ is K_5k_{11} in ref. 6 and was calculated using $k_5/k_{-5}/k_7 = K_5k_7$, $K_5k_7 \cdot k_{11}/k_7 = K_5k_{11}$.

indicates that these dioxygen complexes are extremely labile, which is in accord with their Cu(I) character. On the other hand K_{11} is considerably smaller for $\text{Cu}(\text{CH}_3\text{CN})_2^+$ and $\text{Cu}^{\text{I}}(\text{fum})$ which are considerably weaker reducing agents. Thus the results seem to indicate that K_{11} is controlled by the redox potential of the copper complex, *i.e.* the ability to bind O_2 as $\text{Cu}^{\text{II}}-\text{O}_2^{\cdot-}$.

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