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Mechanism of oxidation of aquated copper(II) ions by hydroxyl free radicals. A high-pressure pulse-radiolysis experiment

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Abstract

The pressure dependence of the reaction $Cu(H_2O)_m^{2+} + {}^{\cdot}OH \rightarrow Cu(III)_{aq} + OH^-$, studied using pulse-radiolysis techniques at pressures up to 150 MPa, suggests a rate-determining ligand interchange mechanism.

The study of the chemical properties of the hydroxyl free radicals is prompted by their role in many deleterious biological processes [1]. The kinetics of oxidation of many transition-metal complexes by hydroxyl free radicals have been studied and are reviewed elsewhere [2]. The mechanisms of these reactions have not been fully elucidated although they have been discussed in detail for many specific systems [3]. This is partly due to the fact that only a limited number of kinetic variables was investigated for such reactions. In recent years, pressure as a kinetic parameter has contributed significantly towards the elucidation of inorganic and organometallic reaction mechanisms [4–6]. Not only can this technique supply additional mechanistic information to that obtained from concentration and temperature dependence studies, but in some cases it presents the only parameter with which the mechanism can really be pin-pointed [7]. It is therefore our intention to use pressure as a mechanistic indicator in reactions involving free radicals, induced by pulse radiolysis, that are significantly slower than diffusion controlled. A series of such studies on homolysis, heterolysis, electron transfer, β-elimination and autoxidation reactions [8] has indicated that these reactions indeed exhibit very significant and characteristic pressure dependencies, which resulted in volumes of activation of between −24 and +24 cm^3 mol^{-1}. We are confident that the observed effects add a further dimension to mechanistic studies dealing with free radical reactions.

As a typical example we investigated the pressure dependence of reaction (1), for which the rate constant at 25 °C and ambient pressure is 3.5×

$$Cu(H_2O)_m^{2+} + {}^{\cdot}OH \xrightarrow{k} Cu(III)_{aq} + OH^- \qquad (1)$$

10^8 dm^3 mol^{-1} s^{-1} [9], which is significantly far away from the diffusion-controlled limit. The pulse-radiolysis work was performed on the linear accelerator at the Hebrew University of Jerusalem using a transportable high pressure unit complete with a four-window pressure cell [10]. N_2O saturated solutions containing 3×10^{-4} mol dm^{-3} Cu^{2+} at pH 6 were irradiated with a 1.5 μs pulse in a pillbox optical cell made of suprasil [11]. This cell was positioned close to the metal window of the modified high pressure cell. Water was used as pressurizing medium and experiments were performed up to 150 MPa pressure. All other experimental details are identical to those described before [12].

Two typical kinetic traces at 0.1 and 150 MPa along with the corresponding first-order plots are presented in Fig. 1. It is clearly seen that these single pulse experiments produce high quality kinetic

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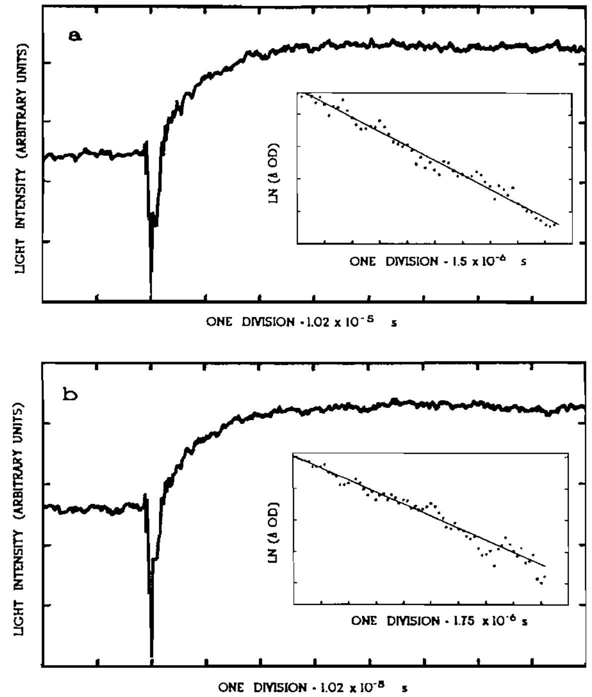

Fig. 1. Computer output of the time dependence of the light transmittance of the sample following the pulse. For experimental conditions see text. (a) Trace recorded at 0.1 MPa pressure. (b) Trace recorded at 150 MPa pressure.

TABLE 1. Pressure dependence of k_{obs}[a]

Pressure (MPa)	$k_{obs} \times 10^{-5}$ (s^{-1})		$\overline{k_{obs}} \times 10^{-5}$ (s^{-1})
0.1	1.18[b]	1.33	1.26±0.06
	1.28	1.21	
	1.29		
75	1.28	1.25	1.22±0.06
	1.25	1.12	
	1.20		
150	1.11	1.31[c]	1.21±0.11
	1.09	1.21	
	1.32		
$\Delta V^{\#}$ (cm^3 mol^{-1})			+0.7±0.2

[a]For experimental conditions see text. [b]Experimental data shown in Fig. 1(a). [c]Experimental data shown in Fig. 1(b).

traces at ambient and elevated pressure, and demonstrate that the adopted cell design enables sufficient irradiation to reach the sample.

The experimental results are summarized in Table 1, from which it follows that the rate constant exhibits no significant dependence on pressure within the experimental error limits over the pressure range investigated. The corresponding volume of activation was estimated from the slope ($= -\Delta V^{\#}/RT$) of a plot of ln k versus pressure in the usual way [4]. Although this value is practically zero, it is of mechanistic significance as will be seen from the following discussion.

Four different mechanisms have been proposed for the oxidation of transition-metal complexes by hydroxyl free radicals.

(a) An outer-sphere electron-transfer process, probably via the formation of an encounter complex as shown in eqn. (2).

$$\begin{array}{rcl} \mathrm{M(H_2O)}_m^{\,n+} + \cdot\mathrm{OH} & \overset{K}{\rightleftharpoons} & \{\mathrm{M(H_2O)}_m^{\ n+}, \cdot\mathrm{OH}\} \\ & & \downarrow k_{\mathrm{ET}} \\ & & \mathrm{M(H_2O)}_m^{(n+1)+} + \mathrm{OH}^- \end{array} \tag{2}$$

This mechanism was ruled out since the observed second-order rate constant Kk_{ET} disagreed with that expected on the basis of the Marcus theory [13, 14].

(b) An inner-sphere electron-transfer process as outlined in eqn. (3). This mechanism was ruled out for many systems, but not for reaction (1),

$$\begin{array}{rcl} \mathrm{M(H_2O)}_m^{\,n+} + \cdot\mathrm{OH} & \overset{K}{\rightleftharpoons} & [\mathrm{(H_2O)}_{m-1}\ \mathrm{M(OH)}]^{n+} + \mathrm{H_2O} \\ & & \downarrow k_{\mathrm{ET}} \\ & & [\mathrm{(H_2O)}_{m-1}\ \mathrm{M}^{(n+1)+}(\mathrm{OH}^-)]^{n+} \\ & & \downarrow \mathrm{H}^+ \\ & & \mathrm{M(H_2O)}_m^{(n+1)+} \end{array} \tag{3}$$

since the overall rate of the reaction is often faster than the rate of the inner-sphere ligand exchange of $\mathrm{M(H_2O)}_m^{\,n+}$. For both the rate-determining electron-transfer mechanisms outlined in eqns. (2) and (3), it is reasonable to expect a significant increase in rate constant with increasing pressure [15]. The observed second order rate constant k is a composite function ($k = Kk_{ET}$) such that $\Delta V^{\#}(k) = \Delta \bar{V}(K) + \Delta V^{\#}(k_{ET})$ in both cases. The value of $\Delta \bar{V}(K)$ is expected to be close to zero, whereas $\Delta V^{\#}(k_{ET})$ should be significantly negative due to an increase in electrostriction during charge creation. In addition, oxidation of a metal center usually results in a significant intrinsic volume decrease [16]. It is therefore realistic to expect a significantly negative volume of activation for a process involving charge creation.

(c) After ruling out the outer- and inner-sphere electron transfer mechanisms for some oxidations of aqua complexes by hydroxyl radicals, Berdnikov [13] proposed a hydrogen-atom abstraction mechanism as outlined in eqn. (4) (the oxygen atom on the hydroxyl radical is tagged to distinguish this reaction from the one presented in eqn. (5)).

$$\begin{array}{lcl} M(H_2O)_m{}^{n+} + \cdot O^*H & \longrightarrow & [(H_2O)_{m-1}\,M(OH)]^{n+} + H_2O^* \\ & & \quad\downarrow \\ & & [(H_2O)_{m-1}\,M^{(n+1)+}(OH^-)]^{n+} \\ & & \quad\downarrow H^+ \\ & & M(H_2O)_m{}^{(n+1)+} \end{array} \qquad (4)$$

Here again we expect a significantly negative volume of activation since the hydrogen abstraction is according to this suggestion facilitated by a strong interaction with the metal cation, i.e. the hydrogen abstraction step involves a partial oxidation of the central metal cation.

(d) Alternatively an inner-sphere electron-transfer mechanism in which the penetration of the hydroxyl radical into the coordination sphere of the metal cation (i.e. substitution) is the rate-determining step, can be envisaged. In this mechanism (5) the subsequent electron transfer step is fast and will not affect the pressure dependence of the overall process

$$\begin{array}{lcl} M(H_2O)_m{}^{n+} + \cdot O^*H & \xrightarrow{k} & [(H_2O)_{m-1}\,M(O^*H)]^{n+} + H_2O \\ & & \quad\downarrow \\ & & [(H_2O)_{m-1}\,M^{(n+1)+}(O^*H^-)]^{n+} \\ & & \quad\downarrow H^+ \\ & & M(H_2O)_m{}^{(n+1)+} \end{array} \qquad (5)$$

(the oxygen atom on the hydroxyl radical is tagged to distinguish this reaction from the one presented in eqn. (4)). This reaction will be characterized by a $\Delta V^{\#}$ value typical for ligand substitution and solvent exchange reactions on the metal cation. In the case of Cu(II) complexes, solvent exchange and complex formation reactions are characterized by small positive volumes of activation typical for an I_d mechanism [17, 18]. We conclude that the zero pressure effect observed for the reaction of aquated Cu(II) with $\cdot OH$ can be assigned to the operation of a rate-limiting ligand substitution mechanism, most probably of the interchange (I_d) type. The less positive value found in this study as compared to the quoted solvent exchange and complex formation reactions may indicate that the smaller hydroxyl radical (entering ligand) requires a smaller metal–water bond elongation than required in the latter cases.

We conclude that high-pressure pulse-radiolysis experiments can add a new dimension to resolving the intimate mechanisms of free radical reactions in inorganic and organometallic chemistry.

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