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Oxygenation of Metal Complexes: On Mechanistic Details of Initial Interaction

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Temperature perturbations of both anaerobic and oxygenated solutions of the square planar complexes of cobalt, rhodium and iridium, $[M(L\text{–}L)_2]^+$ (M = metal atom, L–L = diphosphine chelate), produce identical small changes in their visible spectra. These observations, together with rate law and activation energy data, provide no evidence for any chemically significant intermediates during the formation of the previously established peroxo complexes, $[(O_2)M(L\text{–}L)_2]^+$, from molecular oxygen and $[M(L\text{–}L)_2]^+$.

The reversible formation of dioxygen–metal complexes (eqn. 1) [1, 2], and the autoxidation of metal ions (*e.g.*, eqn. 2) [3] have often been considered to proceed *via* an intermediate O_2 adduct or "dot complex" (eqn. 3). The nature of this species has usually not been specified, but it has been assumed [3] or postulated [4] that the adduct represents a true intermediate which precedes an electron transfer from metal to molecular oxygen (eqn. 2, 3), that is to say that the "dot" [5] implies an initial coordination of *neutral* dioxygen to the metal or some kind of chemical O_2–M association.

$$ML_i + O_2 \rightleftharpoons (O_2)ML_i \qquad (1)$$

(M = central metal atom; L_i = ligands)

$$Fe^{II}(aq.) + O_2 \rightleftharpoons (O_2)\cdot Fe^{II}(aq.) \longrightarrow Fe^{III}(aq.) + O_2^- \qquad (2)$$

$$M^{n+} + O_2 \rightleftharpoons (O_2)\cdot M^{n+} \longrightarrow \text{oxygenation–oxidation products} \qquad (3)$$

We have inquired into this fundamental mechanistic question by re-examining the oxygenation kinetics of some synthetic complexes (eqn. 4) [6] using a combined stopped-flow and temperature-jump apparatus [7]. The results, detailed below, have given no evidence for the existence of a *chemically significant* $O_2\cdot M$ adduct prior to oxygenation–oxidation of these complexes (eqn. 4).

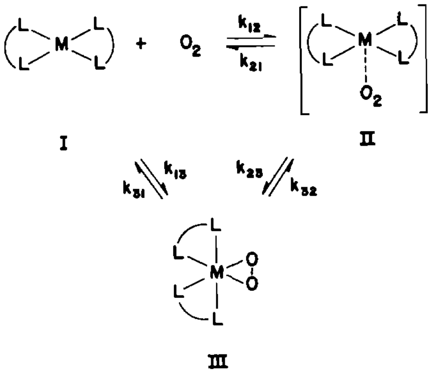

Figure 1. A diagram for the reversible oxygenation of metal complexes: M = Co, Rh, Ir; L–L = PC=CP, see eqn. 4; k = rate constant. **I**: square planar $[M(PC{=}CP)_2]^+$ [6]; **II**: possible "dot" intermediate (see text, eqn. 3); **III**: formally octahedral $[(O_2)M(PC{=}CP)_2]^+$ [8].

$$[M^{I}(PC{=}CP)_2]^+ + O_2 \rightleftharpoons [(O_2)M^{III}(PC{=}CP)_2]^+ \qquad (4)$$

(M = Co, Rh, Ir; PC=CP = *cis*-$(C_6H_5)_2PCHCHP(C_6H_5)_2$

A general reaction scheme for the reversible oxygenation of planar ML_4 type compounds leading to monomeric peroxo complexes, $(O_2)ML_4$ (eqn. 4), may be formulated as depicted in Figure 1 [8]. Previous dynamic studies on these [6] and related systems [9] suggested that the formation of the oxygenated products (**III**) is best interpreted as a one-step process (k_{13}). Entropy and Linear Free Energy Relationships (LFER) correlations [6, 9] have given evidence for a transition state structure closely resembling the dioxygen complexes (**III**). However, a possible rapid pre-equilibrium step involving a "dot" intermediate (**II**), whose formation is likely to be a diffusion-controlled process, could not be discounted on the basis of these data.

Accordingly, experiments were designed to test the above hypothesis. Table I summarizes the visible spectral data [10] for the starting materials, and the kinetic and activation parameters for their oxygena-

TABLE I. Electronic Spectral Data (E, a) for [M(PC=CP)$_2$]Cl in Degassed Ethanol (10^{-4} M in Complex) Containing 0.1 M [(CH$_3$)$_4$N]Cl; Kinetic (k_{13}, Second-order Rate Constant), Activation Enthalpy (ΔH^*_{13}) and Entropy (ΔS^*_{13}) Parameters for the Oxygenation of [M(PC=CP)$_2$][B(C$_6$H$_5$)$_4$] in Chlorobenzene; All Data at 25 °C; see eqn. 4 and Figure 1 [10–12][a].

Complex, M	E, kK	a, M^{-1} cm^{-1}	k_{13}/M^{-1} sec^{-1}	ΔH^*_{13}/kcal	ΔS^*_{13}/eu
Co[b]	16.4	(810)	1.7×10^4	4.3	−25
Rh[c]	21.2	200			
	24.9	4830	0.10	13	−18
Ir[b]	19.1	380			
	22.8	2240	0.42	6.4	−39
	26.5	2530			

[a] Throughout this paper it is assumed that the observed kinetic and thermodynamic data correspond to reaction I → III in Fig. 1; thus, subscripts 13 and 31 are used for the experimental values; see text. [b] These oxygenations are essentially irreversible; rough estimates for equilibrium constants, K_{13} (= k_{13}/k_{31}, Fig. 1): Co, 10^9; Ir, 10^6 M^{-1}. [c] Deoxygenation: k_{31}, 3.0×10^{-4} sec^{-1}; ΔH^*_{31}, 24 kcal; ΔS^*_{31}, 7 eu. Thermodynamics of oxygenation: ΔH^o_{13}, −11 kcal; ΔS^o_{13}, −25 eu; ΔG^o_{13}, −3.5 kcal; K_{13}, 330 M^{-1}.

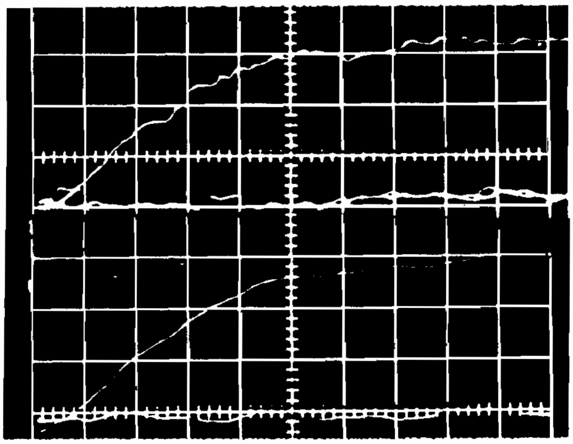

Figure 2. The effect of a 12 kV jump on ethanol solutions ([(CH$_3$)$_4$N]Cl, 0.1 M):

[Rh(PC=CP)$_2$]Cl, M	O$_2$, M	Vertical axis	Horizontal axis
Upper curve:			
1.7×10^{-4}	4.1×10^{-3}	5 mV/div	2×10^{-5} sec/div
Lower curve:			
3.4×10^{-4}	–	10 mV/div	2×10^{-5} sec/div

tion [11, 12]. This process (eqn. 4) is accompanied by a substantial decrease or virtual disappearance of the spectral absorptions. Temperature jump perturbations were applied, at 25 °C, to ethanol solutions containing [(CH$_3$)$_4$N]Cl (0.1 M), O$_2$ (10^{-3}–10^{-2} M; P_{O_2}, 325–725 mm) and [M(PC=CP)$_2$]Cl (10^{-4}–10^{-3} M) [13]; the oxygen–metal complex ratios (O$_2$:M) ranged from 1 to 50 in different experiments (typically, O$_2$:M = 10–30). The perturbations (*ca.* 3.1–4 °C increase) were introduced at various intervals after mixing the reagents (eqn. 4) [14], and the spectra of the complexes were recorded at each of the maxima (Table I) [10] for a duration of *ca.* 10^{-4}–10^{-3} sec. In every case, except for the cobalt complex [15], a single relaxation effect was observed, with a time constant $\tau_H = 3 \times 10^{-5}$ sec which was established to be the heating time. The absorbances decreased by 0.9–3.7%, depending on the conditions and complexes used, but *identical small spectral changes* were recorded when the same temperature jump was applied to solutions of [M(PC=CP)$_2$]Cl in the *absence of oxygen* (rigorously deoxygenated solutions) [16]. These spectrophotometric changes probably arise from temperature-dependent molar absorptivities, as suggested by separate experiments [17–19]. Typical oscilloscope traces are shown in Fig. 2.

The data summarized in this paper, together with the following arguments, suggest that a "dot" or "outer sphere complex" is, if it "exists", of negligible importance in the oxygenation of [M(PC=CP)$_2$]$^+$, and probably also of related square planar d^8 compounds [9] which yield six-coordinate peroxo complexes [1] (**III**, Fig. 1).

(1) Species **II** (or any other analogous adduct) implies an electronic interaction between the metal and O$_2$, and would thus be expected to exhibit a spectrum considerably different from the starting materials (**I**), by analogy with the well-established five-coordinate adducts of these metals with neutral molecules [20]. An analysis of the temperature jump data corresponding to the fast effect provided no evidence for a **II**-like species within the limits of the detection sensitivity of our instrument ($\Delta A \cong 10^{-4}$, Fig. 2) [7]. An undetectable relaxation amplitude [21] could also result from a very small equilibrium constant, K_{12} (= $k_{12}/k_{21} \cong 1$ M^{-1}), and, on electrostatic grounds, K_{12} may indeed be expected to be <1 M^{-1}, since molecular oxygen is an uncharged reactant [22].

However, a very low K_{12} would mean that the hypothetical pathway, I → II → III, plays an insignificant role in the oxygenation process, I → III.

(2) The observed pseudo first order rate constant, k_{obs}, for the reaction scheme in Figure 1 is derived to yield the expression given in eqn. 5, assuming $k_{21} \gg k_{23}$, and a steady state concentration of **II**.

$$k_{obs} = \frac{(k_{13} + k_{23}K_{12})([O_2])}{1 + K_{12}([O_2])} + k_{31} + k_{32} \tag{5}$$

Accordingly, k_{obs} should increase linearly with $[O_2]$ at relatively low oxygen concentrations, and become independent of the latter at high $[O_2]$ values. Such a saturation effect has not been observed. A plot of k_{obs} (25 °C) for the oxygenation of the rhodium complex *vs.* $[O_2]$ (O_2:Rh = 43–107) was linear throughout the range studied. The same first order dependence on oxygen has been found for the reactions of related compounds [9].

(3) A consideration of the activation enthalpies (ΔH^*) also seems relevant. If the hypothetical intermediate **II** were of chemical significance, the observed ΔH^* would be composed of ΔH°_{12} (the thermodynamic enthalpy change for **I** → **II**) and ΔH^*_{23} (Fig. 1). The formation of **II** is expected to be a diffusion-controlled reaction with $\Delta H^\circ_{12} \cong 2$–$3$ kcal [23], and ΔH^*_{23} and ΔH^*_{13} are likely to be of comparable magnitude, considering the similar stereochemical changes accompanying these processes, **II** → **III** and **I** → **III**. For the oxygenation of the cobalt complex, the observed activation enthalpy (ΔH^*_{13} in Table I) is already small, and route **I** → **II** → **III** would thus predict an unreasonably low value for ΔH^*_{23}.

The present study has obviously not provided an unequivocal answer to the question of the existence of a "dot" intermediate in the oxygenation–oxidation of metal complexes at large (eqn. 3). The presence of a vanishingly small concentration of **II**, in combination with $k_{23} \gg k_{13}$ (eqn. 5), could make an experimental detection of **II** a difficult process. The negative evidence includes the observation that the temperature jumps did not detectably alter the equilibria (eqn. 4) which apparently derives from the very slow kinetics of these deoxygenation reactions (Table I) [12]. The method employed here will be extended to investigate the oxygen-carrying mechanisms of iron and cobalt complexes of biological significance [2].

Acknowledgment

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5 "Dot formulas" (*e.g.*, eqn. 2, 3) abound in chemical literature for a variety of compounds whose structures or bonding properties have not been established. The meaning or interpretation of the "dot" seems to range from a "normal covalent bond" through a "loose association" (*e.g.*, "water of crystallization") to an activated complex with no energy minimum.

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10 The spectral data in Table I include only the maxima (*E*) which were suitable for temperature jump measurements. Each of the complexes exhibits at least three bands in the visible region (see Ir), but those excluded from Table I appear as shoulders [6]. For cobalt, the well-defined absorption, *E* = 13.8 kK was beyond the range of the temperature jump instrument, and the band cited (16.4, Table I) is actually a shoulder whose extinction coefficient is uncertain. There are no significant differences between the spectra of the chloride complexes in ethanol in the presence of $[(CH_3)_4N]Cl$ (Table I) and the $B(C_6H_5)_4^-$ salts in chlorobenzene [6].

11 Preliminary kinetic data of these reactions have been reported previously [6]. The results in Table I represent redetermined values by the same spectrophotometric methods (conventional: Ir, Rh; stopped flow; Co; 10–40 °C). Standard deviations are in the same range as given previously [6, 9]. Subscripts 13 and 31 for the kinetic and thermodynamic parameters (Table I) correspond to subscripts 2 and −1, respectively, in the earlier paper [6].

12 The reversible oxygenation of the chloride complex, $[Rh(PC{=}CP)_2]Cl$, was studied also in ethanol in the presence of 10^{-1} *M* $[(CH_3)_4N]Cl$, *i.e.*, in the same environment as used for temperature jump measurements. Results (for conditions and units, see Table I): k_{13}, 0.083; ΔH^*_{13}, 9.5; ΔS^*_{13}, −32; k_{31}, 9.8×10^{-5}; ΔH^*_{31}, 22; ΔS^*_{31}, −2.5; ΔH°_{13}, −13; ΔS°_{13}, −29; ΔG°_{13}, −4.1; K_{13} (= k_{13}/k_{31}), 850. Thus, there is only a relatively minor anion and/or solvent effect (mainly entropic), Cl^- in ethanol (above) *vs.* $B(C_6H_5)_4^-$ in chlorobenzene (Table I).

13 Temperature jump measurements require polar solvents for a supporting electrolyte. Our oxygen-carrying organometallic complexes [1, 6, 8, 9] are, however, insoluble in water and most of them also in alcohols, the chloride salts used in this study representing the few exceptions. Yet, the latter compounds are more difficult to isolate and handle than their alcohol-insoluble derivatives (*e.g.*, $B(C_6H_5)_4^-$ salts) which have formed the basis for structural [8] and dynamic [6, 11] characterization of these complexes. Of the three cations (M = Co, Rh, Ir),

$[Rh(PC{=}CP)_2]^+$ has been found to be most amenable to present mechanistic investigations because its oxygenation is readily reversible (Table 1) [12].

14 Co, 0.02 sec–2 min; Rh, 5 min–22 days; Ir, 5 min–5 hr. These times range from instances at which the oxygenation is still in progress [15] to those corresponding to equilibrium values (Table I) [12].

15 At ambient conditions, the oxygenation of $[Co(PC{=}CP)_2]^+$ is essentially complete within *ca.* 0.04–0.05 sec. In one experiment, the jump was applied to a solution estimated to contain about 24% unoxygenated cobalt (0.02 sec after mixing the reagents, O_2:Co = 1.4, *via* stopped flow), but no spectral change was observed. Under these conditions, the hypothetical "dot complex" (eqn. 3; **II**, Fig. 1), if it existed, should have been at its maximum concentration (see text). A one % absorbance decrease was recorded for an oxygen-free Co solution.

16 No spectral changes were observed when temperature jumps were applied to blank ethanol solutions containing *only* $[(CH_3)_4N]Cl$, establishing that the small absorbance alterations derive from the metal complexes employed.

17 The magnitude of the absorbance (A) decrease of the oxygen-free solutions of $[M(PC{=}CP)_2]Cl$ increased with (a) the voltage of the applied jump and (b) the concentration of the complexes (*i.e.*, the % ΔA was approximately constant), and the change varied slightly with the spectral maxima (E, Table I). In all cases, ΔA was reversible: as the cell cooled, A returned to the initial (pre-jump) value (*ca.* 3 min). The temperature-dependence of the spectrum of $[Rh(PC{=}CP)_2]Cl$ was examined also by conventional spectrophotometric methods. The A of the 24.9 kK band decreased by *ca.* 7% on heating the solution from 25 to 40 °C, and, on cooling to 25 °C, reverted to approximately the original value. This change roughly agrees with the corresponding temperature jump observations ($-\Delta A$ = 2.6%, +4 °C) assuming a linear relationship between A and temperature, and considering the different methods of measurements and the experimental errors involved.

18 In a previous study of the electronic spectra of $[M(PC{=}CP)_2]Cl$ (M = Ir, Rh) [19], a large increase in absorbance maxima (but not in integrated intensity) was observed upon cooling the solutions of the complexes from 25° to −196°C. These absorbance changes (estimated from the graphs in ref. [19]) are, approximately, in agreement with our data on ΔA [17]. The two lowest energy spectral bands (Table I) have been assigned to metal-to-ligand charge-transfer transitions [19].

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20 The visible spectra of square pyramidal (*cf.* **II**) SO_2- and trigonal bipyramidal CO complexes of these and related univalent Ir and Rh species, $(X)ML_4$ (X = SO_2 or CO), are entirely different from those of their planar precursors (ML_4), as expected when the coordination number of a d^8 metal changes from four to five. (i) SO_2: (a) L. Vaska and S. S. Bath, *J. Am. Chem. Soc., 88,* 1333 (1966); (b) J. Peone, Jr., *Ph.D. Dissertation,* Clarkson College of Technology, 1971 (and references cited therein). (ii) CO: (a) L. Vaska, *Science, 152,* 769 (1966); (b) [9c] and references given.

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