Mechanism of Cobalt Dithiolene Complex Catalysis of Thiol Autoxidation in Acidic Acetonitrile Solution

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Summary The efficient catalysis by $[Co(mnt)_2]_2^{2-}$ (mnt ≡ maleonitriledithiolate) of the reaction $2PhCH_2SH + O_2 \rightarrow PhCH_2SSCH_2Ph + H_2O_2$ in acetonitrile, acid-buffered with excess of $PhMe_2N/PhMe_2NH^+ClO_4^-$, is described; the mechanism involves sequential co-ordinative activation of thiol and oxygen, the reactive intermediate being $PhMe_2NH{-}{-}O_2{-}[Co(mnt)_2]_2{-}SCH_2Ph^{2-}$.

In the homogeneous catalysis by transition metal systems of the autoxidation of substrates with active hydrogen, three fundamental mechanistic questions arise, (i) whether there is activation of substrate or oxygen, or both, by co-ordination at a transition metal site; (ii) whether the catalyst centre undergoes a change in oxidation level during catalysis; and (iii) whether the redox steps proceed by e^- or H° transfer.[1]

We have investigated in detail reaction (1) as it is catlysed by $[Co(mnt)_2]_2^{2-}$ [2] in acetonitrile solution, in the

$$2PhCH_2SH + O_2 \longrightarrow PhCH_2SSCH_2Ph + H_2O_2 \qquad (1)$$

presence of excess of $PhNMe_2$ and $PhNMe_2H^+ClO_4^-$ functioning as non-co-ordinating Brønsted acid–base buffer components.† The following significant results permit characterisation of the mechanism type.

1. (a) There is no autoxidation in the absence of the catalyst. (b) In the presence of $[Co(mnt)_2]_2^{2-}$ molecular oxygen is rapidly consumed‡ and disulphide produced according to the stoicheiometry of equation (1). There is no irreversible conversion of $[Co(mnt)_2]_2^{2-}$, except for a very slow decomposition (not greater than one mole per cent of substrate turnover), apparently due to the product hydrogen peroxide. Thus $[Co(mnt)_2]_2^{2-}$ functions as a strongly accelerative and cleanly regenerative catalyst.

2. (a) The rate increases with the concentrations of both buffer components, and decreases with increasing concentration of inert salt ($Bu^n_4P^+ClO_4^-$). (b) For wide ranges of reactant concentrations the initial rate (R_{obs}) of autoxidation, evaluated as the steady state rate after the short (*ca.* 5 s) transient, is described by equation (2),§ with all four denominator terms experimentally significant.

$$R_{obs} = -\,d(pO_2)/dt = C_0[X]_T[PhCH_2SH]_T pO_2/(C_1 + C_2pO_2 + C_3[PhCH_2SH]_T + C_4[PhCH_2SH]_T pO_2) \qquad (2)$$
$$X \equiv [Co(mnt)_2]_2^{2-}$$

3. (a) The electronic spectrum of $[Co(mnt)_2]_2^{2-}$ in acetonitrile is unchanged by the buffer components, oxygen, or all three together. (b) In the presence of all reactants, on initiation of catalysed autoxidation, there are

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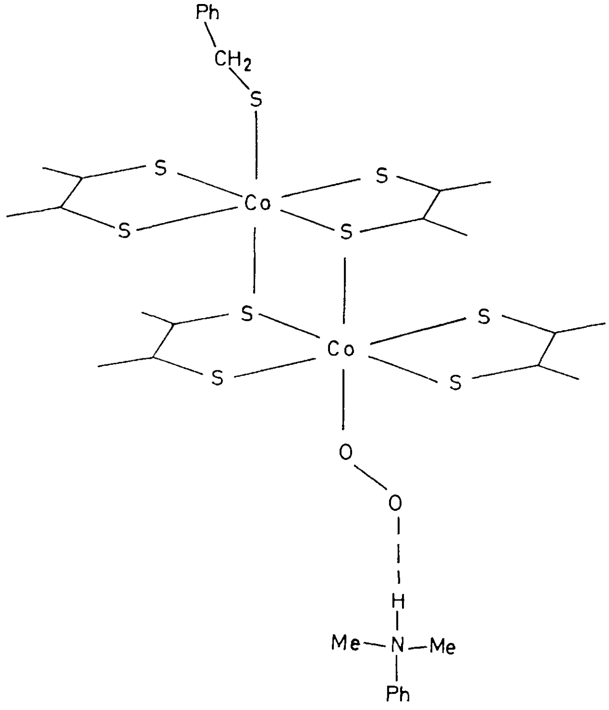
† Aqueous $pK_a = 5{\cdot}15$: deprotonation of benzylthiol is insignificant in this buffer.

‡ Typical reaction: $[Co(mnt)_2]_2^{2-}$, 5×10^{-4}M; $PhCH_2SH$, $2{\cdot}5 \times 10^{-2}$M, $pO_2 = 675$ Torr; $PhNMe_2$ and $PhNMe_2H^+ClO_4^-$ both 0·1M; $T = 18$ °C: initial rate of oxygen consumption = 0·11 μmol O_2 per ml of solution per second; oxygen and thiol consumption half complete in 55 s, complete in 250 s.

§ The subscript T denotes total concentration. At 18 °C, $C_1/C_0 = 2{\cdot}1 \times 10^{-3}M^2$ s, $C_2/C_0 = 1{\cdot}06 \times 10^{-5}M^2$ Torr^{-1} s, $C_3/C_0 = 4{\cdot}2 \times 10^{-2}$M s, $C_4/C_0 = 3{\cdot}1 \times 10^{-4}$M Torr^{-1} s.

changes in the spectrum of $[Co(mnt)_2]_2^{2-}$. These spectral changes develop as rapidly as autoxidation turnover, and are followed by slow reversion to the spectrum of $[Co(mnt)_2]_2^{2-}$ during thiol consumption. (c) The rapid initial spectral intensity changes are linearly proportional to R_{obs}.

4. (a) In the absence of oxygen, addition of thiol to $[Co(mnt)_2]_2^{2-}$ in $PhNMe_2/PhNMe_2H^+ClO_4^-$ buffered acetonitrile produces rapid ($t_{1/2}$ typically less than 5 s) spectral changes (different from those in the presence of oxygen), the concentration dependence of which is consistent with formation of an adduct between $[Co(mnt)_2]_2^{2-}$ and a thiol species. (b) Following this adduct formation there is a slow reduction to $[Co(mnt)_2]_2^{2-}$. (c) Under comparable conditions the rate of this reduction ($d[Co(mnt)_2^{2-}]/dt$) in the absence of oxygen is less by a factor of at least 10 than the rate ($-d[PhCH_2SH]/dt = -2d[O_2]/dt$) of autoxidation in the presence of oxygen.



FIGURE

5. The rate of autoxidation is strongly inhibited by added Ph_3P, in proportion to the formation of the adduct $[Ph_3PCo(mnt)_2]^-$.

The interpretation of observations 3, 4(a), and 5 is that $[Co(mnt)_2]_2^{2-}$ (with two vacant co-ordination sites) remains dimeric in this buffer system and does not co-ordinate oxygen alone, but does co-ordinate base activated thiol, which co-ordination then promotes oxygen co-ordination (requiring acid activation). Ping-pong mechanisms[3] for catalysis, involving complementary electron-transfer reactions of the two oxidation states of the catalyst, can be eliminated from consideration on the basis either of observation 4(c) or the form of the rate equation. The mechanism of equations (3)—(8) is suggested ($B \equiv PhNMe_2$, $BH^+ \equiv PhNMe_2H^+$, $RSH \equiv PhCH_2SH$, $X \equiv [Co(mnt)_2]_2$).

$$RSH + B \overset{K_1}{\rightleftharpoons} RSHB \tag{3}$$

$$X^{2-} + RSHB \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X\text{–}SR^{3-} + BH^+ \tag{4}$$

$$BH^+ + O_2 + X\text{–}SR^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} BH\text{–}O_2\text{–}X\text{–}SR^{2-} \tag{5}$$

$$BH\text{–}O_2\text{–}X\text{–}SR^{2-} \xrightarrow{k_4} B + HO_2^{\circ} + X^{2-} + RS^{\circ} \tag{6}$$

$$HO_2^{\circ} + RSH \xrightarrow{\text{fast}} H_2O_2 + RS^{\circ} \tag{7}$$

$$2RS^{\circ} \xrightarrow{\text{fast}} RSSR \tag{8}$$

With the reasonable assumption that process (3) maintains equilibrium, and the steady state approximation for $X\text{–}SR^{3-}$ and $BH\text{–}O_2\text{–}X\text{–}SR^{2-}$, the calculated initial rate takes the form of equation (2).

Strong support for this mechanism (ordered sequential co-ordination[3]) derives from analysis of the empirical equation in terms of the steady state concentrations of co-ordinative intermediates, equations (9), (10). Equation (10) accounts for the observed linear relationship between the rate and spectral changes during catalysis.

$$[X\text{–}SR^{3-}]_{SS}/[X]_T = (R_{obs}/pO_2[X]_T) \times C_3/C_0 \tag{9}$$

$$[BH\text{–}O_2\text{–}X\text{–}SR^{2-}]_{SS}/[X]_T = (R_{obs}/[X]_T) \times C_4/C_0 \tag{10}$$

$$X \equiv [Co(mnt)_2]_2$$

From experimental values of C_3/C_0 and C_4/C_0, $[X\text{–}SR^{3-}]_{SS}/[X]_T$ and $[BH\text{–}O_2\text{–}X\text{–}SR^{2-}]_{SS}/[X]_T$ range from 0·40 to 0·007 and 0·52 to 0·02, respectively.

If $BH\text{–}O_2\text{–}X\text{–}SR^{3-}$ has the structure shown in the Figure, the direction of electron density shift in the key step is $RS^- \rightarrow [Co(mnt)_2]_2^{2-} \rightarrow O_2 \rightarrow {}^+HNMe_2Ph$. The function of the dithiolene complex catalyst is to activate both reductant and oxidant by co-ordination, and transmit one electron from the former to the latter. There is precedent for this concept in the co-ordination chemistry of oxygen with cobalt chelate complexes.[4] However, the balance of co-ordinative and electron-transfer functions appropriate for optimal catalysis of autoxidation occurs infrequently. To the extent that comparisons are possible, thiol autoxidation catalysis by $[Co(mnt)_2]_2^{2-}$ under the acidic conditions reported here appears to be more efficient than by other non-enzymatic transition metal catalysts.[5]

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