Kinetics and Mechanism of Oxidation of Diaqua[2,2-difluoro-5,6,12,13-tetramethyl-1,3-dioxa-4,7,11,14-tetra-aza-2-boracyclotetradeca-4,6,11,13-tetraene(1—)-*NN′N″N‴*]cobalt(II) Perchlorate

By **Renata Dreos, Gianni Tauzher,** and **Giacomo Costa,** Istituto di Chimica, Universita di Trieste, Trieste, Italy
Michael Green,* Department of Chemistry, University of York, Heslington, York YO1 5DD

The kinetics and mechanism of irreversible oxidation of the title complex in water by oxygen have been studied. The process is accelerated by halide ions and by increase in acidity. A comparison is made with oxymyoglobin.

‘ AUTOXIDATION ’, the process whereby an FeO_2 complex is irreversibly transformed into an iron(III) system is an important feature of the chemistry of iron porphyrins, myoglobin, and haemoglobin. Like iron(II), many cobalt(II) complexes react with oxygen to form hyperoxo-complexes.[1-11] In several ways the systems resemble each other, the latter providing models for biochemical counterparts of the former; one of the most spectacular comparisons is the similarity between haemoglobin and coboglobin.[12] In this paper the ‘ autoxidation ’ of a Co^{II} complex is studied.

High-spin Co^{II} complexes react reversibly with oxygen to form chiefly dicobalt peroxo-complexes.[1] These tend to change irreversibly in the presence of H^+ into

---

[1] For a review see A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1969, **13**, 1.

[2] B. M. Hofmann, D. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[3] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[4] M. Green and D. Mettrick, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 149. A factor of 100 was omitted here. Hence at 25 °C, K_1 (with respect to dissolved O_2) in dmf = 53 ± 7 l mol^{-1}; thus taking the solubility of O_2 in dmf as 4.76 mol l^{-1}, K_1 (with respect to gaseous O_2) = 0.25 ± 0.03 atm^{-1} (D. Mettrick, Thesis, York University, 1969).

[5] G. Amiconi, M. Brunori, E. Antonini, G. Tauzher, and G. Costa, *Nature*, 1970, **228**, 549.

[6] E. W. Abel, J. M. Pratt, and R. Whelan, *Inorg. Nuclear Chem. Letters*, 1971, **9**, 901.

[7] H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 1559.

[8] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

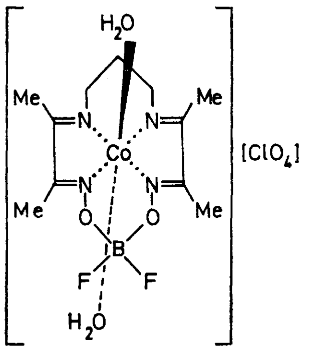
[9] F. A. Walker, *J. Amer. Chem. Soc.*, 1973, **75**, 1154.

[10] G. Tauzher, G. Amiconi, M. Brunoni, E. Antonini, and G. Costa, *Nature* (*New Biology*), 1973, **241**, 222.

[11] D. V. Stynes, H. C. Stynes, J. A. Ibers, and B. R. James, *J. Amer. Chem. Soc.*, 1973, **95**, 1142, 1796.

[12] B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci.*, 1970, **67**, 637.

more stable Co^{III} complexes. A better model for myoglobin is provided by low-spin Co^{II} complexes which react with oxygen (again reversibly) to form monocobalt hyperoxo-species also.[2-11] In protic media an irreversible 'autoxidation' process may then occur. We present here the results of a kinetic study on one such Co^{II} system in which the reaction with oxygen and subsequent formation of a stable Co^{III} complex was followed. The complex used was diaqua[2,2-difluoro-5,6,12,13-tetramethyl-1,3-dioxa-4,7,11,14-tetra-aza-2-boracyclotetradeca-4,6,11,13-tetraene(1—)-*NN'N''N'''*]cobalt(II) perchlorate, $[Co(OH_2)_2(dtct)][ClO_4]$. It is water soluble and sufficiently stable to be studied over the concentrations of hydrogen and halide ions used here without substitution, protonation, or deprotonation occurring.



RESULTS

The reaction of $[Co(OH_2)_2(dtct)][ClO_4]$ in aqueous solution with oxygen was followed spectrophotometrically. The reaction is catalysed by chloride, bromide, and iodide ions, in increasing order of effectiveness, and also by nitrite and thiocyanate ions. It is dependent on hydrogen-ion concentration.

Although halogeno-complexes are formed to some extent in solutions saturated with halide ions,[13] at the concentrations used here the aqua-complex is the principal species present (representing at least 99% of the reactant). The products are $[Co(OH_2)_2(dtct)]^{2+}$, $[Co(OH_2)X(dtct)]^+$, or $[CoX_2(dtct)]$ depending on halide-ion concentration, $[X^-]$. Precipitation of the dihalogeno-complexes (which are neutral and of low solubility) places an upper limit on the concentrations of halide ions that can be used.

Runs were made at 25.0 ± 0.05 °C at 1M ionic strength maintained with sodium nitrate.* Initial concentrations of cobalt complexes were less than 0.5×10^{-5}M throughout, small compared with those of other reactants. Linearity in plots of log concentration against time indicated a reaction which was first order in cobalt concentration (see Experimental section). First-order rates constants so found, $k_{obs.}$, where $-d[Co(OH_2)_2(dtct)^+]/dt = k_{obs.}[Co(OH_2)_2(dtct)^+]$, were linearly related to the halide-ion concentration over the following ranges of molarity: $0 \leqslant [Cl^-] \leqslant 0.2$; $0 \leqslant [Br^-] \leqslant 0.1$; and $0 \leqslant [I^-] \leqslant 0.0006$, at fixed $[H^+]$. Finite rate constants were observed when no halide ion was present. Values of $k_{obs.}$ were dependent on pH in the absence and presence of halide ion. Plots of $k_{obs.}$ against $[H^+]$ were curved ($10^{-7} < [H^+] < 0.1$M) but those of $1/k_{obs.}$ against $1/[H^+]$ were approximately linear with finite intercepts.

A qualitative direct relation between $k_{obs.}$ and the concentration of dissolved oxygen was observed. However, difficulty in controlling this concentration precisely in unsaturated solutions prevented quantitative studies from being made. The discussion below is based on experiments with solutions saturated with oxygen and assuming a first-order dependence of the rate on $[O_2]$.

The 'main' reactions (1) and (2) lead at steady state to the rate equation (A) (where k_{main} is a hypothetical analogue of $k_{obs.}$) and hence to (B) and (C).

$$[Co(OH_2)_2(dtct)]^+ + X^- + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [CoX(O_2)(dtct)] + 2H_2O \qquad (1)$$

$$[CoX(O_2)(dtct)] + H^+ \xrightarrow{k_2} \text{Products} \qquad (2)$$

$$-\frac{d[Co(OH_2)_2(dtct)^+]}{dt} = \frac{k_1k_2[Co(OH_2)_2(dtct)^+][H^+][O_2][X^-]}{k_{-1} + k_2[H^+]} \qquad (A)$$

$$k_{main} = \frac{k_1k_2[H^+][O_2][X^-]}{k_{-1} + k_2[H^+]} \qquad (B)$$

$$\frac{1}{k_{main}} = \frac{k_{-1}}{k_1k_2[H^+][O_2][X^-]} + \frac{1}{k_1[O_2][X^-]} \qquad (C)$$

The linear relations between $k_{obs.}$ and $[X^-]$ at constant $[H^+]$ and between $1/k_{obs.}$ and $1/[H^+]$ at fixed $[X^-]$ are compatible with (B) and (C) respectively. However, the finite intercept dependent on pH observed in the first of these plots when $[X^-] = 0$ points to the 'background' reactions (3) and (4).

$$[Co(OH_2)_2(dtct)]^+ + O_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Co(OH_2)(O_2)(dtct)]^+ + H_2O \qquad (3)$$

$$[Co(OH_2)(O_2)(dtct)]^+ + H^+ \xrightarrow{k_4} \text{Products} \qquad (4)$$

$$k_{background} \text{ or } k_{back.} = \frac{k_3k_4[H^+][O_2]}{k_{-3} + k_4[H^+]} \qquad (D)$$

As before we obtain (D). If $k_{obs.}$ is identified as $(k_{main} + k_{back.})$ and (B) and (D) are added, the linear relation at constant $[H^+]$ between $k_{obs.}$ and $[X^-]$ with its finite intercept is accounted for satisfactorily as in equation (E). Unfortunately the resulting equation shows no apparent simple relation between $1/k_{obs.}$ and $1/[H^+]$. However, the values of k_3 and k_{-3}/k_4 were such that $1/(k_{obs.} - k_{back.})$ also gave an approximately linear plot against $1/[H^+]$.

$$k_{obs.} = \frac{k_1k_2[H^+][O_2][X^-]}{k_{-1} + k_2[H^+]} + \frac{k_3k_4[H^+][O_2]}{k_{-3} + k_4[H^+]} \qquad (E)$$

These preliminary observations suggest that the choice of reactions (1)—(4) is correct. A best fit of all the data to equation (E) was made by minimising χ^2, giving the rate constants in the Table. It was verified using *F* tests that a 'significantly' better fit was obtained by including the background reactions, but not by assuming some pre-equilibrium formation of $[Co(OH_2)X(dtct)]$ as in (1a) below.

Reaction (1), formally written as termolecular, can be replaced by two steps, (1a) and (1b). Provided $k_{-1a} \gg k_{1b}[O_2]$, $k_1 \equiv K_{1a}k_{1b}$ and $k_{-1} \equiv k_{-1b}$ in equations (A), (B), (C), and (E), and in the Table. Step (1) may also be split into the

---

* 1M = 1 mol dm^{-3}, 1 atm = 101 325 Pa.

[13] M. Green and G. Tauzher, unpublished work; *Transition Metal Chem.*, 1975, **1**, 1.

bimolecular reactions, (3) and (5), which suggests a possible alternative overall scheme. A steady-state treatment of (2)—(5) leads to (F). No justification could be found statistically for fitting our data to an equation like (F) containing terms in $[H^+]^2$ and in $[X^-]$ in its denominator. Thus if (F) is to be fitted, it is necessary, since $k_{-3} \gg k_4[H^+]$, that $k_{-5} \gg k_2[H^+]$ and that $k_2k_5[H^+][X^-]$ is small, whence (G) results.

Values of rate constants at 25.0 °C and $I = 1$M; errors are 67% confidence limits (*i.e.* standard deviations corrected for the number of observations)

X	$\frac{k_1}{l^2\,mol^{-2}\,s^{-1}}$	$\frac{k_{-1}/k_2}{mol\,l^{-1}}$	$\frac{k_1k_2/k_{-1}}{l^3\,mol^{-3}\,s^{-1}}$
I^-	6 530 ± 730	(2.52 ± 0.75) × 10^{-3}	(2.58 ± 0.70) × 10^{6}
Br^-	9.44 ± 0.40	(3.66 ± 0.36) × 10^{-3}	2 570 ± 230
Cl^-	342 ± 25	0.99 ± 0.09	345 ± 19

	$\frac{k_3}{l\,mol^{-1}\,s^{-1}}$	$\frac{k_{-3}/k_4}{mol^{-1}}$	$\frac{k_3k_4/k_{-3}}{l^2\,mol^{-2}\,s^{-1}}$
	5.70 ± 0.29	0.616 ± 0.045	9.3 ± 0.54

$$[Co(OH_2)_2(dtct)]^+ + X^- \underset{k_{-1a}}{\overset{k_{1a}}{\rightleftharpoons}} [Co(OH_2)X(dtct)] \quad (1a)$$

$$[Co(OH_2)X(dtct)] + O_2 \underset{k_{-1b}}{\overset{k_{1b}}{\rightleftharpoons}} [CoX(O_2)(dtct)] + H_2O \quad (1b)$$

$$[Co(OH_2)(O_2)(dtct)] + X^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} [CoX(O_2)(dtct)] \quad (5)$$

$$k_{obs.} = \frac{k_3k_4[O_2][H^+]}{k_{-3} + k_4[H^+] + k_5[X^-] - \{k_{-5}k_5[X^-]/(k_{-5} + k_2[H^+])\}} + \frac{k_2k_3k_5[O_2][X^-][H^+]}{(k_{-3} + k_4[H^+] + k_5[X^-])(k_{-5} + k_2[H^+]) - k_{-5}k_5[X^-]} \quad (F)$$

$$k_{obs.} = \frac{k_2k_3k_5[O_2][X^-][H^+]}{k_{-3} + k_4[H^+]} + \frac{k_3k_4[O_2][H^+]}{k_{-3} + k_4[H^+]} \quad (G)$$

Equation (E), which fits the data well, is only equivalent in mathematical form to (G) if $k_{-1}/k_2 = k_{-3}/k_4$. The Table shows that there is at least a 98% confidence that this equality is not true for Cl^- with even larger values for Br^- and I^-. Thus scheme (1)—(4) cannot justifiably be replaced entirely by (2)—(5). *F* Tests show that if the two schemes occur simultaneously the former provides the path for at least 30, 99, and 99% of the overall reactions for Cl^-, Br^-, and I^- respectively. Thus (5) is unimportant both for Br^- and I^-; for simplicity it is assumed that the same is true for Cl^- in the data in the Table.

DISCUSSION

The choice of reactions (1)—(4) for the mechanism of oxidation of $[Co(OH_2)_2(dtct)]^+$ seems justified in principle, but some amplification and comment are needed. Reaction (1) has been split into (1a) and (1b). The complex $[Co(OH_2)X(dtct)]$ can certainly be detected in solution at high concentrations of halide ion by visible and e.s.r. spectroscopy [13] and it is formed within the mixing time. Perhaps the tabulated value of k_1 (X = Cl) is out of sequence because it is, in fact, made up of both k_1 and $k_2k_3K_5/k_4$, *cf.* (E) and (G). Alternatively the irregularity could arise because k_1 is composed of two terms (*viz.* $k_1 = K_{1a}k_{1b}$) the first of which decreases in the sequence chloride, bromide, iodide and the second of which increases. Support for the last suggestion is provided by the facts that in the sort of hyperoxocobalt complex discussed here the O_2 group is more like a hyperoxo- than a dioxygen ligand, and that donor power increases on going from chloride to iodide. (Unfortunately the changes in neither the visible nor the e.s.r. spectra were sufficiently great for K_{1a} to be estimated accurately.)

Evidence for the monocobalt hyperoxo-species is provided by e.s.r. spectroscopy.[13] Solutions of $[Co(OH_2)_2(dtct)][ClO_4]$ in *NN*-dimethylformamide–water (9:1) through which oxygen had been bubbled for 1 min, at 25 °C, on quenching to 77 K showed a spectrum very similar to those of related [2,6] CoO_2 complexes, presumably due to $[Co(OH_2)(O_2)]^+$. Very slightly different spectra in the presence of halide ions provides evidence for $[CoX(O_2)]$. Incidentally, the kinetics described here provide no evidence for a dicobalt peroxo-species (*cf.* refs. 11 and 13), as rates of reaction are strictly first order in cobalt complex concentration.

Unfortunately the experiments do not give k_2 and k_4, but they do provide values for K_1k_2 and K_3k_4 which represent rate constants for the overall irreversible oxidation process at low $[H^+]$ where (2) and (4) which involve H^+ are rate determining. These overall rate constants increase with the donor power of the ligand ***trans*** to the co-ordinated oxygen, in the order Cl^-, Br^-, I^-, which is logical as positively charged H^+ ions are being consumed.

The immediate products of (2) and (4) can only be speculated on. If hydrogenperoxocobalt complexes [containing a $Co(O_2H)$ unit] are formed they are very probably short lived, since there is no evidence for them from the e.s.r. studies [13] mentioned above nor is there any indication from the kinetics here that (2) and (4) are reversible, as would be observed if these complexes were acidic and relatively stable. It is difficult to devise a plausible subsequent scheme based on a reaction between a hydrogenperoxocobalt and a Co^{II} species. Therefore the choices are that any hydrogenperoxocobalt complexes rapidly decompose to $HO_2\cdot$ and cobalt(III)-containing complexes or that these products are formed directly in reactions (2) and (4), *viz.* equations (6) or (7). However,

$$[Co^{II}(O_2)] + H^+ \underset{slow}{\rightleftharpoons} [Co(O_2H)]^+ \xrightarrow[fast]{} Co^{III} + HO_2\cdot \quad (6)$$

$$[Co^{II}(O_2)] + H^+ \longrightarrow Co^{III} + HO_2\cdot \quad (7)$$

there is one snag. There is no evidence for a chain process: no induction period or change of order with time, no capricious irreproducibility, and no fractional order of reaction {other than that at high $[H^+]$ which we have explained much more satisfactorily in terms of the reversible reactions (2) and (4)}; nor does there seem to be a plausible chain which will give an order of one in cobalt complex concentration. To meet these difficulties, it seems reasonable to suggest that $HO_2\cdot$ reacts much as it would in an iron(II) system, *viz.* equations (8)—(11). {Hydrogen peroxide has not been detected, but the rate constant for the reaction $[Co(OH_2)_2(dtct)]^+ + H_2O_2$ is *ca.* 10 l mol^{-1} s^1, which in this context is large.}

One of the most interesting implications in connection with comparable Fe^{II} oxygen-carrying systems is that

$$Co^{II} + HO_2\cdot \longrightarrow Co^{III} + HO_2^- \quad (8)$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \quad (9)$$

$$Co^{III} + H_2O_2 \longrightarrow Co^{III} + OH\cdot + OH^- \quad (10)$$

$$Co^{II} + OH\cdot \longrightarrow Co^{III} + OH^- \quad (11)$$

this Co^{II} complex is an oxygen carrier providing no H^+ is present. This may be compared with the fact that the rate of conversion [14] of oxymyoglobin to iron(III) myoglobin increases with decreasing pH. However, the comparison between the systems cannot be pushed too far. The order of the reaction of the cobalt complex in $[H^+]$ is one at low $[H^+]$, but those of three oxymyoglobins are fractional (0.70, 0.84, and 0.84). Secondly, the rates of conversion of the oxymyoglobins are inversely related to the pressure of oxygen, but that of our CoO_2 complex (once formed) is independent of it.

EXPERIMENTAL

Diaqua[2,2-*difluoro*-5,6,12,13-*tetramethyl*-1,3-*dioxa*-4,7,-11,14-*tetra-aza*-2-*boracyclotetradeca*-4,6,11,13-*tetraene*(1−)-NN′N″N‴]*cobalt*(II) *Perchlorate*, $[Co(OH_2)_2(dtct)][ClO_4]$.—The complex dibromo(10-hydroxyimino-3,9-dimethyl-4,8-diazaundeca-3,8-dien-2-one oximato-*NN′N″N‴*)cobalt(II) (4 g) [15] and $Et_2O\cdot BF_3$ (2.5 cm³) in diethyl ether (50 cm³) were stirred for 24 h. The ether was evaporated and $[Co(dtct)]Br_2$ collected and recrystallised from acetone–water. The complex (3 g) so formed was suspended in water (5 cm³) to which $Ag[NO_3]$ (1.8 g) was added. To the filtrate, slightly less than the stoicheiometric amount of $Na[BH_4]$ was added at 0 °C under nitrogen. The desired complex was precipitated on adding excess of $Na[ClO_4]$ (Found: C, 27.5; H, 4.8; N, 12.0. $C_{11}H_{22}BClCoF_2N_4O_8$ requires C, 27.4; H, 4.6; N, 11.6%). The molar conductivity of the complex is 97.5 S cm² mol⁻¹ as expected for a 1 : 1 electrolyte. The Beer–Lambert law is obeyed over the range of concentrations used for the kinetics.

Kinetics.—The reaction was monitored by following changes in absorbance at 18 000 cm⁻¹ with a Unicam SP 700 spectrophotometer. Pseudo-first-order rate constants were obtained by plotting $\log[(A_t - A_\infty)/(A_0 - A_\infty)]$ against time, where A denotes absorbance and the subscripts time. Anions were added as their sodium salts, and H^+ as perchloric acid. Solutions of oxygen were prepared by shaking water under oxygen at a particular pressure. Ionic strengths were adjusted using $Na[NO_3]$. The solubility of O_2 in 1M-$K[NO_3]$ is 9.32×10^{-4} mol l⁻¹ at 25 °C under 1 atm.[16] The same value was assumed for 1M-$Na[NO_3]$.

[5/020 *Received*, 6*th January*, 1975]

---

[14] W. D. Brown and L. B. Mebine, *J. Biol. Chem.*, 1969, **244**, 6696.

[15] G. Costa, G. Mestroni, and E. de Savorgnani, *Inorg. Chim. Acta*, 1969, **3**, 323.

[16] Landolt-Börnstein, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Springer-Verlag, Berlin, 1962, band 2, part 2, p. 165.