

## A Comparison of Kinetic Data for the Reactions of Superoxo-bridged Dicobalt Complexes with Iodide in Aqueous Perchloric Acid Solutions

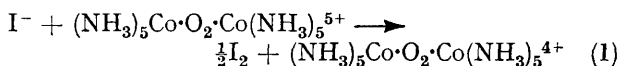
By R. Davies and A. G. Sykes, Department of Inorganic and Structural Chemistry, The University, Leeds 2

The kinetics of the one-equivalent reactions of the superoxo-complexes  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$ ,  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$ , and  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  with iodide have been studied in aqueous perchloric acid solutions made up to  $\mu = 2.0\text{M}$  with  $\text{LiClO}_4$ . A large excess of iodide was used so that first-order kinetics were observed. At constant hydrogen-ion concentrations, pseudo-first-order rate constants  $k_{\text{obs}}$  give the following dependence on  $[\text{I}^-]$ :  $k_{\text{obs}} = a[\text{I}^-]^2 + b[\text{I}^-]$  where at  $[\text{H}^+] = 0.01\text{M}$  and  $1.4^\circ$ ,  $a = 1.21$ ,  $12.5$ , and  $350\text{ l. mole}^{-1}\text{ sec.}^{-1}$  and  $b = 0.0024$ ,  $0.11$ , and  $0.60\text{ l. mole}^{-2}\text{ sec.}^{-1}$  for the complexes  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$ ,  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$ , and  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  respectively. Ion-pair formation (which is rapid) is believed to precede electron transfer in both cases. By varying the hydrogen-ion concentration over the range  $0.01$  to  $2.0\text{M}$  it has been shown that each of the terms in  $a$  and  $b$  can be split into  $[\text{H}^+]$ -independent and direct  $[\text{H}^+]$ -dependent terms.

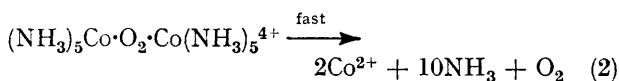
In preliminary runs on the reaction of iodide with the tri-bridged superoxo-complex  $(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2\text{OH}, \text{O}_2)\cdot\text{Co}(\text{NH}_3)_3^{3+}$  at  $25^\circ$  and  $[\text{H}^+] = 0.01\text{M}$ , overall rates are slower (by a factor of about fifty) than for the reaction of the mono-bridged complex. The reaction is much more rapid at higher hydrogen-ion concentrations however. The negative charge associated with the three bridging ligands is probably an important factor in explaining these rates.

THE kinetics of one-equivalent reductions of four superoxo-bridged dicobalt complexes with iodide are reported. In these reactions the cobalt atoms may be assumed to remain in oxidation state (III) throughout, the reactions being essentially a one-equivalent reduction of the bridging ligand,  $\text{O}_2^- + e \longrightarrow \text{O}_2^{2-}$ . Findings in the case of the single-bridged complex are essentially as obtained previously<sup>1</sup> in  $\text{HClO}_4$ - $\text{NaClO}_4$  media except that one of the terms in  $[\text{H}^+]$  is somewhat smaller.<sup>†</sup> In other redox reactions of binuclear complexes of cobalt the interpretation of data has to some extent depended on whether lithium or sodium perchlorate has been used to adjust the ionic strength.<sup>3</sup> Results obtained using lithium perchlorate are generally the more reliable.

*Reaction of  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  with Iodide.*—The procedure was as before.<sup>1</sup> Reduction of the superoxo-complex as in equation (1), is followed by the rapid



decomposition (2) of the peroxo-complex. By using a



large excess of iodide the reaction could be studied under first-order conditions. The reaction was followed at the superoxo-peak at  $670\text{ m}\mu$  ( $\epsilon = 890$ ). At a constant hydrogen-ion concentration the dependence of pseudo-first-order rate constants,  $k_{\text{obs}}$ , on the iodide concentration is as in equation (3). On varying the hydrogen-ion

$$k_{\text{obs}} = a[\text{I}^-]^2 + b[\text{I}^-] \quad (3)$$

concentration each of the  $a$  and  $b$  terms can be split into  $[\text{H}^+]$ -independent and  $[\text{H}^+]$ -dependent terms, as in (4).

$$k_{\text{obs}} = a_1[\text{I}^-]^2 + a_2[\text{H}^+][\text{I}^-]^2 + b_1[\text{I}^-] + b_2[\text{H}^+][\text{I}^-] \quad (4)$$

<sup>†</sup> At the time of the earlier work<sup>1</sup> the superoxo-complexes were referred to as peroxodicobalt(III, IV) complexes. Following recent X-ray crystallographic studies<sup>2</sup> the superoxodicobalt(III, III) terminology is now preferred.

Values obtained for  $k_{\text{obs}}$  at  $1.4^\circ$  and  $25^\circ$  are given in Table 1.

TABLE I  
Kinetic data for the reaction of iodide with  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  in  $\text{HClO}_4$ - $\text{LiClO}_4$  solutions ( $\mu = 2.0\text{M}$ )

Temp.	$[\text{H}^+]\text{M}$	$10^4[\text{Complex}]\text{(M)}$	$10^2[\text{I}^-]\text{(M)}$	$k_{\text{obs}}\text{(sec.}^{-1}\text{)}$
1.4	0.01	1.31	1.64	0.00038
		5.89	2.00	0.00053
		1.31	2.46	0.00076
		5.89	3.00	0.00108
		1.31	3.28	0.00145
		1.31	4.10	0.00209
		5.89	5.11	0.00329
		5.89	6.20	0.00471
	0.01	2.81	0.492	0.000648
		2.81	0.989	0.00221
		2.81	1.58	0.00494
		2.81	2.47	0.0111
		2.81	2.96	0.0149
		2.81	3.95	0.0264
	1.00	2.02	3.90	0.0281
		2.02	2.92	0.0159
		2.02	2.45	0.0119
		2.02	1.57	0.0054
		2.02	0.975	0.0024
		2.02	0.488	0.00081
	1.97	1.71	4.00	0.0329
		1.71	3.00	0.0193
		1.71	2.50	0.0137
		1.71	1.60	0.0066
		1.71	1.00	0.0027
		1.71	0.501	0.00098

In  $\text{HClO}_4$ - $\text{LiClO}_4$  media the hydrogen-ion independent terms are  $a_1 = 14.9\text{ l.}^2\text{ mole}^{-2}\text{ sec.}^{-1}$  and  $b_1 = 0.062\text{ l. mole}^{-1}\text{ sec.}^{-1}$  at  $25^\circ$ . Previous values in  $\text{HClO}_4$ - $\text{NaClO}_4$  media ( $\mu = 2.0\text{M}$ ) are in good agreement:  $a_1 = 14.6\text{ l.}^2\text{ mole}^{-2}\text{ sec.}^{-1}$  and  $b_1 = 0.075\text{ l. mole}^{-1}\text{ sec.}^{-1}$  at  $25^\circ$ . Although the hydrogen-ion dependent terms make much less contribution to the overall rate-constant, and errors are correspondingly bigger, there appears to be a quite

<sup>1</sup> A. G. Sykes, *Trans. Faraday Soc.*, 1963, **59**, 1343.

<sup>2</sup> (a) W. P. Schaefer and R. E. Marsh, *J. Amer. Chem. Soc.*, 1966, **88**, 178, and *Acta Cryst.*, 1966, **21**, 735; (b) U. Thewalt and R. E. Marsh, *J. Amer. Chem. Soc.*, 1967, **89**, 6364.

<sup>3</sup> (a) J. Doyle and A. G. Sykes, *J. Chem. Soc. (A)*, 1967, 795; (b) R. Davies and A. G. Sykes, *J. Chem. Soc. (A)*, in the press.

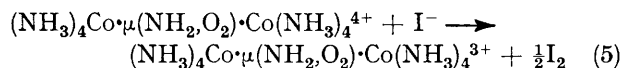
definite effect on  $a_2$  at least in going to  $\text{LiClO}_4$  media. The rate-constants and their estimated accuracies are in Table 5. In previous work it was shown that the reaction was retarded by chloride, the (apparent) equilibrium constant for the formation of ion-pairs between  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  and  $\text{Cl}^-$  being 1.3 l. mole $^{-1}$  at 25°. From results at two temperatures only activation energies corresponding to  $a_1$  and  $b_1$  are 16.1 ( $\pm 1.0$ ) and 21.0 ( $\pm 2.0$ ) kcal. mole $^{-1}$  respectively.

*Reaction of  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  with Iodide.*—The reaction was studied by following the decrease in concentration of the superoxo-complex at

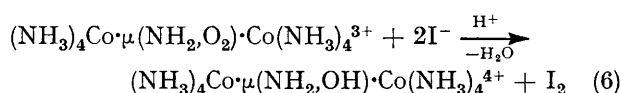
TABLE 2  
Kinetic data for the reaction of  
 $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  with iodide in  
 $\text{HClO}_4\text{--LiClO}_4$  solutions, ( $\mu = 2.0\text{M}$ ;  $[\text{H}^+] = 0.01\text{M}$ )

Temp.	$10^4[\text{Complex}](\text{M})$	$10^2[\text{I}^-](\text{M})$	$k_{\text{obs}}(\text{sec.}^{-1})$
1.4	3.98	0.3201	0.000454
	3.98	0.800	0.0017
	3.98	1.641	0.00601
	3.98	2.462	0.00966
	3.98	4.103	0.0255
25.0	4.34	0.413	0.00721
	3.38	0.530	0.00921
	4.34	0.577	0.0107
	4.34	0.700	0.0140
	3.46	0.775	0.0158
	4.33	0.806	0.0166
	2.53	1.01	0.0224
	4.32	1.01	0.0228

700  $\mu$  ( $\epsilon_{\text{max}} = 306$ ). The peroxo-complex which is formed in the first stage (5) does not absorb at this



wavelength. By using a sufficiently large excess of iodide (at least eight-fold) (Table 2) the subsequent reaction of the peroxo-complex with iodide (6) can be ignored. In this



reaction there is in effect further reduction of the  $\text{O}_2^{2-}$ -bridge,  $\text{O}_2^{2-} + 2e \longrightarrow \text{OH}^- + \text{H}_2\text{O}$ . At the lower iodide concentrations first-order plots were linear to ca. 60% completion and in other runs, with a larger excess of iodide, to around 85% completion. This behaviour is consistent with reaction (6) proceeding at a rate comparable with (5). Pseudo-first-order rate constants (Table 2) show the iodide dependence (Figure 1) corresponding to equation (7), which is of the same form as observed previously for  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$ . The hydrogen-ion dependence was not in this case studied.

$$k_{\text{obs}} = a[\text{I}^-]^2 + b[\text{I}^-] \quad (7)$$

At  $[\text{H}^+] = 0.01\text{M}$  values of  $a$  and  $b$  are assumed to correspond to  $a_1$  and  $b_1$ ; thus at 1.4°  $a_1 = 12.5 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$  and  $b_1 = 0.105 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . From results at two temperatures activation energies for  $a_1$  and  $b_1$  are 12.2 ( $\pm 1.0$ ) and 16.6 ( $\pm 1.0$ ) kcal. mole $^{-1}$  respectively.

The effect of adding quantities of chloride up to 0.10M at  $[\text{H}^+] = 0.01\text{M}$  has also been studied (Table 3).

TABLE 3

The effect of chloride ions on the reaction of  
 $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  with iodide in  $\text{HClO}_4\text{--LiClO}_4$  ( $\mu = 2.0\text{M}$  at 25°;  $[\text{H}^+] = 0.01\text{M}$ )

$10^4[\text{Complex}](\text{M})$	$10^2[\text{I}^-](\text{M})$	$[\text{Cl}^-](\text{M})$	$k_{\text{obs}}(\text{sec.}^{-1})$
4.883	1.008	—	0.0228
4.08	1.008	0.02	0.0224
4.05	1.008	0.04	0.0219
3.95	1.008	0.06	0.0219
—	1.008	0.10	0.0208 <sup>a</sup>
4.22	0.332	0.10	0.00533
4.18	0.413	0.10	0.0067
3.91	0.530	0.10	0.0096
4.15	0.577	0.10	0.0102
4.15	0.700	0.10	0.0131
3.83	0.775	0.10	0.0151
4.08	0.826	0.10	0.0160
2.32	1.008	0.10	0.0205
4.08	1.008	0.10	0.0212

<sup>a</sup> Obtained from a graph of  $k_{\text{obs}}/[\text{I}^-]$  against  $[\text{I}^-]$  by use of other data at  $[\text{Cl}^-] = 0.10\text{M}$ .

The chloride ions retard the reaction as indicated in Figure 1. Whereas  $b_1$  is little affected by the addition of

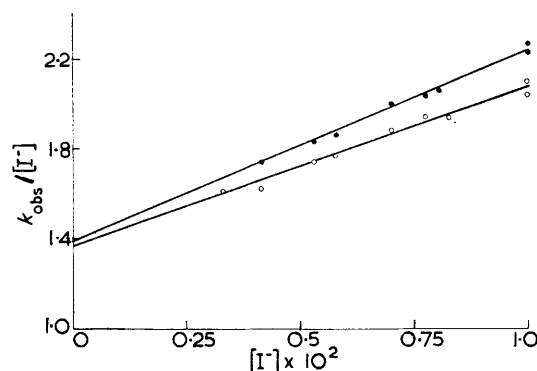


FIGURE 1 The iodide-ion dependence of pseudo-first-order rate constants,  $k_{\text{obs}}(\text{sec.}^{-1})$ , for the reaction of iodide with  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  at  $[\text{H}^+] = 0.01\text{M}$ , 25°, and  $\mu = 2.0\text{M}$ . The lower series of points were obtained in the presence of 0.1M-chloride, and demonstrate the retardation produced by chloride

0.1M-chloride (2% decrease) the effect on  $a_1$  is more marked (15% decrease) (Table 5). This is as might be expected since the activated complex for  $a_1$  contains two iodide ions while that for  $b_1$  contains only one. If  $k_{\text{obs}}$  and  $k'_{\text{obs}}$  are the overall rate constants with and without the addition of chloride (and at constant iodide), and  $K_{\text{IP}}$  is the constant for the formation of ion-pairs between  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  and chloride, then a relationship (8) can be derived by assuming that chloride

$$k_{\text{obs}}/k'_{\text{obs}} = 1 + K_{\text{IP}}[\text{Cl}^-] \quad (8)$$

ion-pairs do not contribute to the reaction. From a graph of  $k_{\text{obs}}/k'_{\text{obs}}$  against  $[\text{Cl}^-]$  at 25° a value of  $K_{\text{IP}} = 0.94 \pm 0.04 \text{ l. mole}^{-1}$  is obtained. In view of the assumptions which have been made we refer to this and the  $K_{\text{IP}}$  obtained for  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  and chloride<sup>1</sup> as apparent rather than absolute constants for

ion-pair formation. If the constant  $a_1$  rather than  $k_{\text{obs}}$  is considered, the argument here being that it is  $a_1$  rather than  $b_1$  which is affected by chloride, then  $K_{\text{IP}} = 1.8 \text{ l. mole}^{-1}$ .

**Reaction of  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\cdot\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  with Iodide.**—This reaction is considerably faster than those so far considered, and using conventional techniques we could only study the reaction below room temperature. The reaction sequence is essentially as in (5) and (6) where again attention is confined to the first stage,  $\text{O}_2^- + e \longrightarrow \text{O}_2^{2-}$ . Details of the reduction of the peroxo-complex as

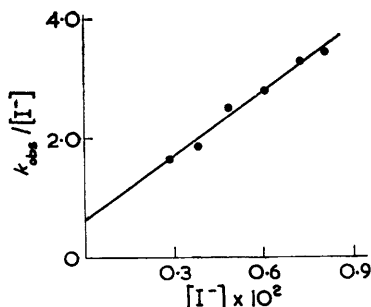


FIGURE 2 The iodide-ion dependence of pseudo-first-order rate constants,  $k_{\text{obs}}$  ( $\text{sec}^{-1}$ ), for the reaction of iodide with  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\cdot\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  at  $[\text{H}^+] = 0.01\text{M}$ ,  $1.4^\circ$ , and  $\mu = 2.0\text{M}$

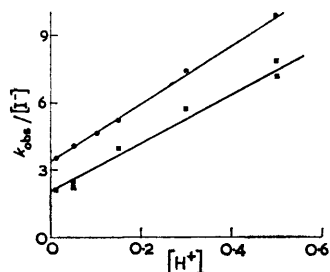


FIGURE 3 The hydrogen-ion dependence of pseudo-first-order rate constants,  $k_{\text{obs}}$  ( $\text{sec}^{-1}$ ), for the reaction of iodide with  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\cdot\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  at  $1.4^\circ$ ,  $\mu = 2.0\text{M}$ , and with  $[\text{I}^-] = 0.008\text{M}$  (upper points) and  $[\text{I}^-] = 0.004\text{M}$  (lower points)

in (6) will be reported elsewhere.<sup>4</sup> The decrease in concentration of the superoxo-complex was followed at the  $687 \text{ m}\mu$  peak ( $\epsilon = 417$ ). The reaction was studied at  $1.4^\circ$ , a large excess of iodide being used. Pseudo-first-order plots were linear to at least 70% and generally to 90% completion, rate-constant  $k_{\text{obs}}$  being shown in Table 4. The iodide dependence is as before (Figure 2). On variation of the hydrogen-ion concentration,  $a$  and  $b$  terms can be split into  $[\text{H}^+]$ -independent and  $[\text{H}^+]$ -dependent terms, (Figure 3) as in equation (4). The hydrogen-ion dependent terms  $a_2$  and  $b_2$  make a more significant contribution than in the reaction of  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  (Table 5). The estimated accuracy of  $a_1$  is  $\pm 6\%$  and of  $a_2$ ,  $b_1$ , and  $b_2 \pm 12\%$ . A second product which we are unable to identify is also formed (*ca.* 10%) and, depending on the nature of the secondary reaction, minor corrections to the rate constants may be necessary.

TABLE 4

Kinetic data for the reaction of  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\cdot\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  with iodide in  $\text{HClO}_4$ - $\text{LiClO}_4$  solutions ( $\mu = 2.0\text{M}$  at  $1.4^\circ$ )

$[\text{H}^+](\text{M})$	$10^4[\text{Complex}](\text{M})$	$10^2[\text{I}^-](\text{M})$	$k_{\text{obs}}(\text{sec}^{-1})$
0.01	3.17	0.282	0.0047
0.01	3.17	0.371	0.0070
0.01	3.17	0.482	0.0121
0.01	3.17	0.599	0.0168
0.01	3.17	0.720	0.0237
0.01	3.17	0.798	0.0276
0.05	1.76	0.400	0.0092
0.05	1.76	0.400	0.0095
0.15	1.76	0.400	0.0156
0.30	1.76	0.400	0.0228
0.50	1.76	0.400	0.0288
0.50	1.76	0.400	0.0312
0.01	3.23	0.800	0.0283
0.05	3.50	0.800	0.0325
0.10	3.74	0.800	0.0373
0.15	1.76	0.800	0.0421
0.30	1.76	0.800	0.0598
0.50	1.76	0.800	0.0784

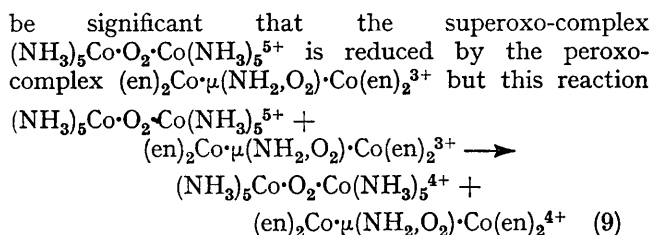
**Reaction of  $(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2\cdot\text{OH}\cdot\text{O}_2)\cdot\text{Co}(\text{NH}_3)_3^{3+}$  with Iodide.**—Preliminary runs at  $\mu = 2.0\text{M}$  and  $[\text{H}^+] = 0.001$  and  $0.01\text{M}$  gave more complex behaviour than was observed in the other reactions, and this investigation remains incomplete. The reaction was followed at the superoxo-peak at  $730 \text{ m}\mu$  ( $\epsilon_{\text{max}} = 206$ ). At  $25^\circ$  and with iodide concentrations  $0.05$ – $0.08\text{M}$  and complex *ca.*  $2 \times 10^{-4}\text{M}$ , pseudo-first-order rate constants were *ca.*  $0.0004 \text{ sec}^{-1}$  ( $[\text{H}^+] = 0.001\text{M}$ ) and *ca.*  $0.0006 \text{ sec}^{-1}$  ( $[\text{H}^+] = 0.01\text{M}$ ). The runs were not always reproducible however, and in some cases there was a slowing and in others a speeding of the reaction after as little as 25% reaction. An explanation of these effects is not obvious and from our limited results we are unable to specify  $[\text{I}^-]^2$  and  $[\text{I}^-]$  terms. Two important points emerge however. First, at the lower hydrogen-ion concentrations the reaction is slower than that of  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  with iodide, and secondly there is a very strong direct hydrogen-ion dependence. At  $25^\circ$  and with  $[\text{H}^+] = 1.5\text{M}$ , for example, the concentration of complex being  $7.3 \times 10^{-4}\text{M}$  and  $[\text{I}^-] = 0.01\text{M}$ , the reaction is complete within 10 min. ( $t_{\frac{1}{2}} = \text{ca. } 150 \text{ sec.}$ ). The spectrum of the product in such a run ( $\epsilon_{\text{max}} = 143$  at  $514 \text{ m}\mu$ ) was obtained by adding tin(II) to remove the iodine produced. In other experiments the iodine was titrated with thiosulphate ( $[\text{H}^+] = 1.8\text{M}$ ), when the overall stoichiometry was found to be 3 : 1. By analogy with the 3 : 1 reaction of iodide with the di-bridged superoxo-complexes,<sup>5</sup> the product is probably  $(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2\cdot\text{OH}\cdot\text{OH})\cdot\text{Co}(\text{NH}_3)_3^{3+}$ . The same product is obtained in the 3 : 1 reaction with ferrous ions.

#### DISCUSSION

Kinetic results are in Table 5. Three factors are believed important in determining the relative rates of these reactions. The first is the free-energy change which will vary as the standard oxidation potential of the superoxo-peroxo-couple varies. There is at present little direct information about such values. It may

<sup>4</sup> R. Davies, A. G. Sykes, and M. B. Stevenson, to be published.

<sup>5</sup> A. G. Sykes and R. D. Mast, *J. Chem. Soc. (A)*, 1967, 784.



is slow ( $t_{\frac{1}{2}} = \text{ca. } 3 \text{ hr.}$  at room temperature),<sup>4</sup> and may only be effective because the mono-bridged peroxo-complex is unstable (10). In other words this reaction

$$(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{4+} \longrightarrow 2\text{Co}^{2+} + \text{O}_2 + 10\text{NH}_3 \quad (10)$$

may not be a true indication of the oxidizing power of the complex  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  relative to  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$ , and the latter could still

rapid. It follows from our interpretation that each of the constants  $a_1$ ,  $a_2$ ,  $b_1$ , and  $b_2$  is a composite term and that each is the product of a rate-constant and at least one stability constant. Activation energies corresponding to  $a_1$  and  $b_1$  have been obtained for the reactions of the complexes  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  and  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$ . These are for  $a_1$  16.1 and 12.2 kcal. mole<sup>-1</sup> and for  $b_1$  21.0 and 16.6 kcal. mole<sup>-1</sup> respectively. Overall activation energy requirements are more favourable therefore in the case of the double-bridged complex.

Although we believe the constants obtained for ion-pair formation between chloride and  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$  ( $K_{\text{IP}} = 1.3 \text{ l. mole}^{-1}$ ) and  $(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$  ( $K_{\text{IP}} = 0.94$ ) to be only approximate, they probably indicate the correct order of magnitude of ion-pairing. Ion-pairing would

TABLE 5

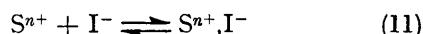
A summary of kinetic data for the reactions of superoxodicobalt complexes with iodide in perchloric acid solutions ( $\mu = 2.0\text{M}$ ). The constants are as defined in the equation  $k_{\text{obs}} = a_1[\text{I}^-]^2 + a_2[\text{H}^+][\text{I}^-]^2 + b_1[\text{I}^-] + b_2[\text{H}^+][\text{I}^-]$

Complex	Temp.	Medium	$a_1$ (l. <sup>2</sup> mole <sup>-2</sup> sec. <sup>-1</sup> )	$a_2$ (l. <sup>3</sup> mole <sup>-3</sup> sec. <sup>-1</sup> )	$b_1$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	$b_2$ (l. <sup>2</sup> mole <sup>-2</sup> sec. <sup>-1</sup> )
$(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$	25°	NaClO <sub>4</sub>	14.6 *	2.7 *	0.075 *	ca. 0.01 *
	25	LiClO <sub>4</sub>	14.9 †	1.35 †	0.062 †	0.022 †
	1.4	LiClO <sub>4</sub>	1.21 †	†	0.0024 §	†
$(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{NH}_3)_4^{4+}$	25	LiClO <sub>4</sub>	85.0 †	†	1.39 † ¶	†
	1.4	LiClO <sub>4</sub>	12.5 †	†	0.105 †	†
$(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$	1.4	LiClO <sub>4</sub>	350 †	525	0.6	8.7

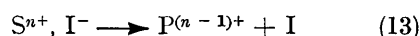
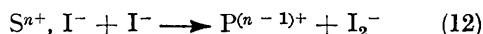
\* Data from ref. 1. † Accuracy  $\pm 5\%$ . ‡ Not studied. § The intercept here is small, estimated accuracy  $\pm 15\%$ . ¶ In the presence of 0.1M-chloride  $a_1 = 72 \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$ , and  $b_1 = 1.36 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ . || Accuracy  $\pm 12\%$ .

be the stronger oxidizing agent. In the reactions of the superoxo-complexes with ferrous ion,<sup>3b</sup> activation energies are essentially the same in all four cases, and this suggests that the overall free-energy changes are either small, or are not important in these reactions,  $\text{O}_2^- + e \longrightarrow \text{O}_2^{2-}$ . The second factor is the ability of the superoxo-complexes to form ion-pairs with iodide, and the third the general accessibility of the superoxo-bridge to the reducing ion. These two factors will now be considered.

That there are terms in  $[\text{I}^-]$  and  $[\text{I}^-]^2$  suggests that in the first step there is ion-pair formation as in (11),



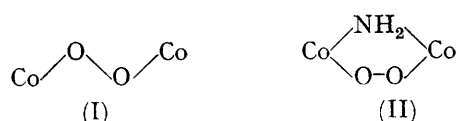
where  $\text{S}^{n+}$  is a superoxo-complex of charge  $n+$ . Subsequent rate-determining steps are then (12) and (13),



where  $\text{P}^{(n-1)+}$  is the corresponding peroxo-complex. Reactions (12) and (13) give rise to terms in  $a$  and  $b$  respectively. The assumption that (11) is rapid and under no circumstances rate-determining makes the approach here simpler than that previously used.<sup>1</sup> Subsequent reactions of the radicals  $\text{I}$  and  $\text{I}_2^-$  to give iodine, and equilibria in which there is protonation of the superoxo-complexes are also assumed to be

certainly be expected to be more favourable for the 5+ complex. In the case of the tri-bridged complex  $(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2\text{OH}_2)\cdot\text{Co}(\text{NH}_3)_3^{3+}$  the presence of three negatively charged bridging groups (and the corresponding decrease in overall charge) would be expected to reduce the extent of ion-pairing. The large  $[\text{H}^+]$ -dependence in both this and the  $(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2\text{O}_2)\cdot\text{Co}(\text{en})_2^{4+}$  reaction seem to draw attention to the more favourable ion-pairing which is possible when there is protonation of (presumably) the superoxo-bridge.

The accessibility of the superoxo-bridge is also believed to be important, the bridge being most shielded in the case of the single-bridged complex  $(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5^{5+}$ . Since ion-pairing would be expected to be more favourable for this 5+ complex, only a fairly large difference in standard oxidation potentials could alternatively account for the *ca.*  $10^3$  difference in rates between the mono- and di-bridged complexes. X-Ray crystallography<sup>2</sup> has shown that there is a different geometric arrangement of the superoxo-bridge in the mono- and di-bridged complexes respectively, as indicated in (I) and (II). Our results are



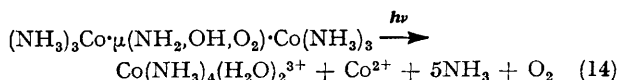


consistent with there being more extensive protonation when the superoxo-bridge is bonded as in (II).

#### EXPERIMENTAL

Samples of  $[(\text{NH}_3)_5\text{Co}\cdot\text{O}_2\cdot\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$ ,  $[(\text{NH}_3)_4\text{Co}\cdot\mu(\text{NH}_2, \text{O}_2)\cdot\text{Co}(\text{NH}_3)_4](\text{NO}_3)_4$ , and  $[(\text{en})_2\text{Co}\cdot\mu(\text{NH}_2, \text{O}_2)\cdot\text{Co}(\text{en})_2](\text{NO}_3)_4$  were prepared by methods as previously described.<sup>5-7</sup> A sample of the tri-bridged complex  $[(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2, \text{OH}, \text{O}_2)\cdot\text{Co}(\text{NH}_3)_3](\text{NO}_3)_3$  monohydrate was prepared as described by Werner.<sup>7</sup> Microanalyses were consistent with the formula  $[(\text{NH}_3)_3\text{Co}\cdot\mu(\text{NH}_2, \text{OH}, \text{O}_2)\cdot\text{Co}(\text{NH}_3)_3]^+(\text{NO}_3)_3\cdot\text{H}_2\text{O}$  (Found: H, 4.85; N, 28.1. Calc. for  $\text{Co}_2\text{N}_{10}\text{H}_{23}\text{O}_{13}$ : H, 4.7, N, 28.6%). When a  $1.5 \times 10^{-3}\text{M}$  solution of the complex in 0.1M-perchloric acid was left in sunlight for 3–5 hr. a photochemically induced decomposition occurred, and oxygen was evolved. The spectrum of the final solution recorded after the solution had been left overnight ( $\epsilon_{\text{max.}} = 60.5$  per mole of dicobalt complex at  $508\text{ m}\mu$ ) is consistent with the formation of one mole of an equilibrium mixture of *cis*- and *trans*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$  ( $\epsilon_{\text{max.}} = 53$  at  $508\text{ m}\mu$ ) and  $\text{Co}^{2+}$  ( $\epsilon_{\text{max.}} = \text{ca. } 5$  at  $500\text{ m}\mu$ ).<sup>\*</sup> There is in addition a small amount of another product which absorbs strongly in the 250–350  $\text{m}\mu$  region. We conclude that the predominant photochemical reaction is (14).

\* It has been reported<sup>8</sup> that the *cis*–*trans* isomerization is fairly rapid ( $t_{\frac{1}{2}} \sim 21\text{ min.}$ ) at  $20^\circ$ . We assume that an equilibrium mixture of *cis* : *trans* (ca. 0.17) is present in both the sample of  $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$  prepared from  $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$  and the reaction product.



On repeating the preparation a sample having an identical visible and u.v. spectrum was obtained. From the kinetic studies reported here and elsewhere,<sup>3b</sup> however, we do not entirely rule out the possibility that there is a small amount of a second component in these samples. Samples of all four superoxo-complexes were stable indefinitely in the dark.

In preparing solutions for runs, flasks containing solutions of the superoxo-complexes were covered with aluminium foil. Reactions were followed spectrophotometrically on a Unicam SP 500 spectrophotometer with a thermostatted cell holder. To start the runs one of the reactants was added from a pipette (in some cases with blowing), and the solutions in the optical cell stirred by a stream of argon passing through a syringe needle. Lithium perchlorate was prepared by adding perchloric acid to lithium carbonate and recrystallised at least three times. All other chemicals used were of AnalaR or equivalent purity.

We thank the S.R.C. for a studentship (to R. D.), and Mr. K. Wailes for help in preparing the complexes.

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<sup>7</sup> A. Werner, *Annalen*, 1910, **375**, 1.

<sup>8</sup> R. G. Yalman and T. Kuwana, *J. Phys. Chem.*, 1955, **59**, 298.