Reactivity of Co-ordinated Oxalate. Part VIII.[1] Further Oxygen-18 Exchange Studies on the Trisoxalatocobalt(III) Anion

By **A. L. Odell** * and **D. B. Rands,** Urey Radiochemical Laboratory, University of Auckland, Private Bag, Auckland, New Zealand

The rate of acid-catalysed exchange of oxygen atoms between solvent water and the trisoxalato-complex of cobalt(III) has been re-investigated. Carbonyl oxygens have been shown to exchange at a greater rate than carboxy oxygens at 25 °C but at higher temperatures carbonyl and carboxy oxygens became kinetically indistinguishable. The significance of this finding in relation to the mechanism of racemisation of trisoxalatocobalt(III) is discussed.

BROOMHEAD *et al.* have recently reported [2] that only 6 of the 12 oxygen atoms in the trisoxalatocobalt(III) anion exchange with water in conflict with the earlier report [3] that all 12 oxygen atoms are kinetically indistinguishable with respect to exchange.† It is noteworthy that the earlier work was carried out at 44·9 °C while Broomhead *et al.* worked at 25 °C. This system has now been re-investigated and the apparent conflict resolved.

EXPERIMENTAL

(*i*) *Preparations and Exchange Runs.*—Methods of preparing materials, carrying out exchange runs, and analysing for oxygen-18 abundances have been previously described.[3]

(*ii*) *Thermal Decomposition.*—Samples of the complex were precipitated from solution as $[Co(en)_3][Co(ox)_3]$ or $[Co(NH_3)_6][Co(ox)_3]$ (where ox represents $C_2O_4^{2-}$) or as the potassium salt on addition of ethanol. Precipitated samples were decomposed by heating them in an evacuated Pyrex tube to just below the softening point of the glass. The precipitate changed from its green-grey colour to black and heating was continued until this colour change appeared complete. The carbon dioxide evolved was trapped in a trap cooled in liquid nitrogen and then distilled from solid carbon dioxide into a sample bulb cooled in liquid nitrogen.

(*iii*) ' *Scrambling* '.—An attempt was made to repeat the observations of Broomhead *et al.*[2] of a ' scrambling ' effect between the two oxygen atoms of the carbon dioxide evolved on heating the complex. No details of experimental procedure were given by Broomhead *et al.* A ' scrambling ' bulb of 200-ml capacity and having a neck 20-cm long was fitted with a platinum wire loop connected to two tungsten leads sealed through the Pyrex walls. This bulb was preconditioned by heating it to 200 °C for 2 h with a heating tape while it was being pumped to *ca.* 10^{-4} Torr. The solid sample was decomposed and the carbon dioxide resulting was led into the ' scrambling ' bulb. (For these studies some 0·5 g of complex was decomposed giving sufficient gas for several mass spectrometric measurements). A small sample was led into the mass spectrometer and the peak-height ratio for $m/e = 44$ and 46 peaks was measured.

The platinum wire was heated electrically to *ca.* 1500 °C for 30 s and then a further small sample was examined. The process was repeated several times on the same specimen of gas. Samples of ^{18}O enriched complex for this study were prepared under conditions ‡ in which the

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† Since this paper was prepared a further communication from Broomhead *et al.*[4] has appeared in which exchange of all twelve oxygen atoms is recognised, with 6 exchanging more rapidly and 6 more slowly.

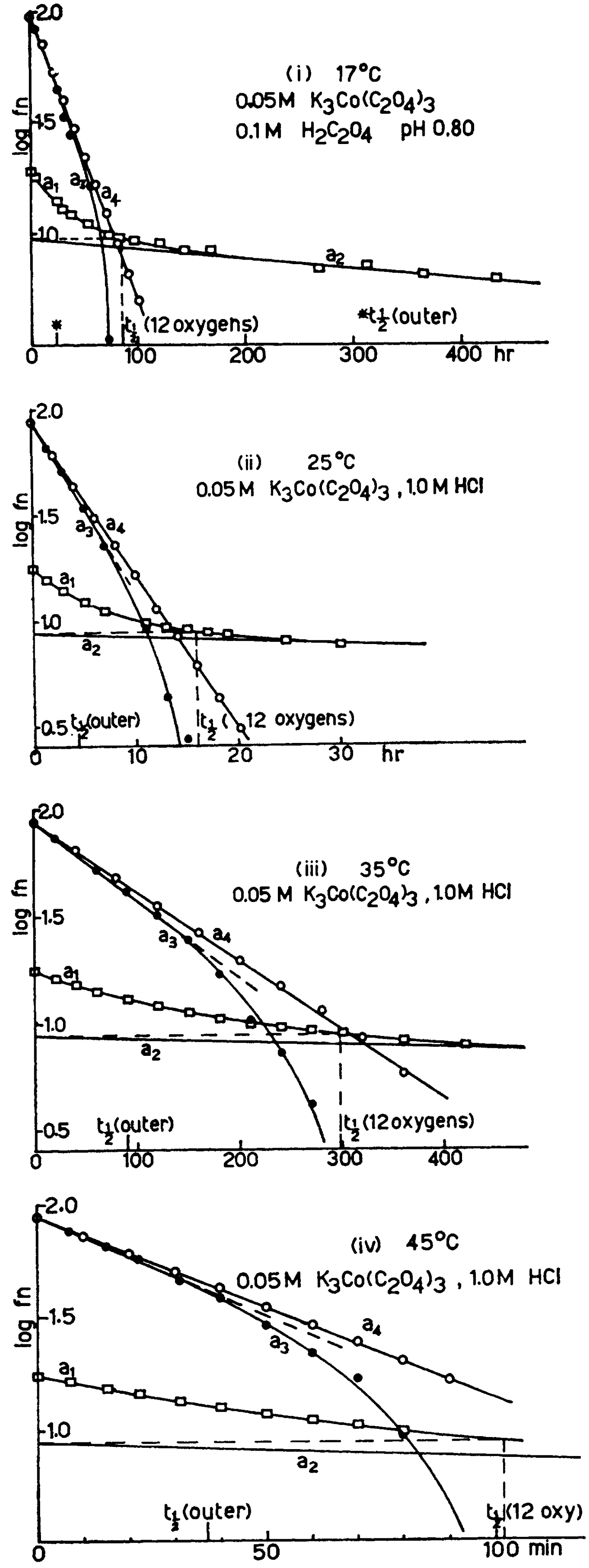
‡ We have shown that there is greater separation between rates of exchange of the two types of oxygen at lower temperatures. Hence ' scrambling ' samples were prepared at various temperatures from 2 to 25 °C.

[1] Part VII, A. L. Odell and D. Shooter, *J.C.S. Dalton*, 1972, 135.

[2] J. A. Broomhead, I. Lauder, and P. Nimmo, *Chem. Comm.*, 1969, 652.

[3] Part I, C. A. Bunton, J. H. Carter, D. R. Llewellyn, Charmian O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 1964, 4615.

[4] J. A. Broomhead, I. Lauder, and P. Nimmo, *J. Chem. Soc.* (*A*), 1971, 645.



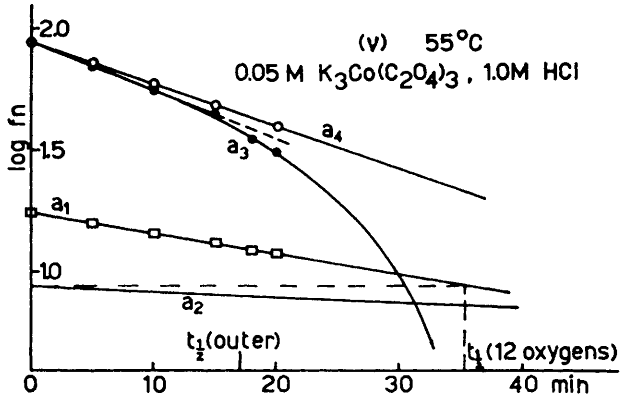


FIGURE 1 log fn for $a_1 = \log(a_\infty - a_t) + 1$

a_2 = limiting slope of a_1, representing inner oxygen exchange.

log fn for $a_3 = \log(\frac{a_\infty + a_0}{2} - a_t) + 2$

log fn for $a_4 = \log[(\text{antilog } a_1 - \text{antilog } a_2)_t] + 2$

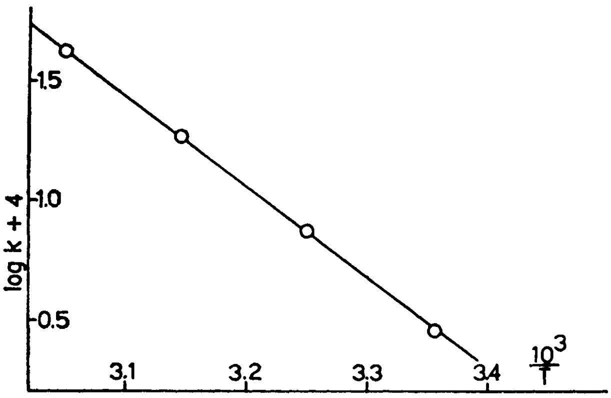


FIGURE 2 Arrhenius plot for outer oxygen exchange. T in °K, [HCl]=1M, $[Co(C_2O_4)_3^{3-}]$ = 0.05M.

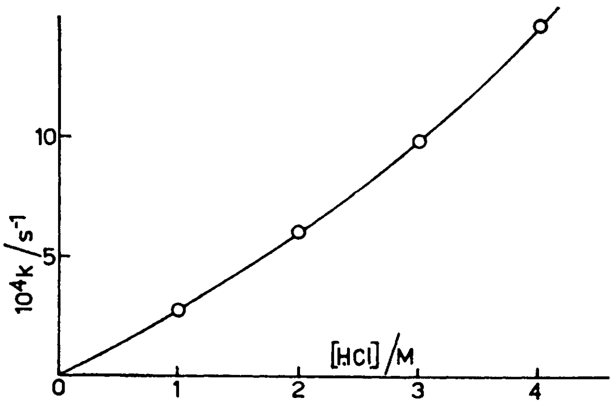


FIGURE 3 Acid dependence of outer oxygen exchange. T=25°C, $[Co(C_2O_4)_3^{3-}]$ = 0.05M

exchange of outer oxygen atoms should have been very much greater than that of inner oxygens.

Preliminary runs carried out with a bulb having a large greased joint near the platinum wire showed a ' scrambling ' effect, the ratio 46 : 44 falling, in a manner similar to that reported [2] earlier, when the apparatus was first assembled. After several runs using different samples of gas, without regreasing the joint, the ratio no longer fell. The final apparatus described above gave much smaller changes in the ratio (less than 1%), and when the preconditioning procedure was thorough, the ' scrambling ' effect was not observable.

Samples of ^{18}O enriched trisoxalatochromate(III) anion were treated in the same way and, again, changes in the 46 : 44 ratio were similar, *viz.* a slight fall but not greater than 1% if careful preconditioning were carried out. This small drop in the ratio is ascribed to traces of air being released into the system from the walls and from the grease of the stopcock as the latter is turned, the effect being enhanced by heat from the hot wire. We conclude that there is no ' scrambling ' effect in the carbon dioxide obtained by thermal decomposition of the cobalt complex and that it is identical in this respect with the chromium complex.

If, in spite of the above considerations, one adjusts the ratios reported below for the 3% ' scrambling ' effect claimed by Broomhead *et al.*[2] the change is too small to account for the discrepancy between the previously reported results.[2,3]

(*iv*) *Conditions of Runs.*—To ensure that results would be comparable with those reported [2,3] earlier it was necessary that runs be performed over an extended temperature range (17—55°). The extent of exchange that could be followed was limited by aquation but at 17, 25, and 35 °C greater than 50% total exchange was pursued [see a_1 Figure 1 (i), (ii), (iii)].

Typical results are in Figure 1, while results for outer, or carbonyl oxygen exchange at various temperatures are in Figure 2, whence $E_{act} = 17{\cdot}2$ kcal/mol and $\log_{10} A = 9{\cdot}1$ in 1M-HCl. Studies on a range of acid concentrations are reported in Figure 3.

DISCUSSION

The earlier conflict of views [2,3] is now resolved. All 12 oxygen atoms do, in fact, exchange with solvent water but there are two kinetically distinguishable groups, each containing 6 oxygen atoms, the 6 ' outer ' oxygens (presumably the carbonyl oxygens) exchanging faster than the 6 ' inner ' oxygens (presumably metal-bound carboxy oxygens). At 45 °C the rates for the two types are almost indistinguishable, while at 25 °C the two rates are very different, carboxyl oxygen exchange being almost negligible.[2] Nevertheless it is clear from Figure 1 [and also from graph (b) in ref. 2] that exchange does proceed beyond 50% showing that exchange of carboxy oxygen atoms does occur at this temperature. The runs carried out at 17 °C show this carbonyl oxygen exchange even more strikingly [Figure 1 (i)].

The presence of two parallel rates processes makes the use (see ref. 2 and a_3 Figure 1) of the simple first-order plot inappropriate and the standard method [5] for two simultaneous first-order processes must be used. A difficulty is that aquation of the complex [6,7] prevents one from obtaining an accurate measure of the limiting slope of the plot of log $(a_\infty - a_t)$ *versus* time (curve a_1 Figure 1) which measured the rate of exchange of the six inner oxygens (a_2 Figure 1). With $\log\left(\frac{a_\infty - a_0}{2}\right)$ as the initial point for this slower reaction one can estimate a half-life [*e.g.* 160 h for curve a_2 Figure 1 (ii)]. With this half-life, and correcting the earlier part of the curve for the secondary exchange, good linear plots (a_4 Figure 1) were obtained. In contrast, it can be seen that with exchange proceeding beyond 50% exchange of 12 oxygens the treatment of the data as for a simple first-order exchange involving only 6 oxygens [graph (b) in ref. 2] gives a non-linear plot which becomes asymptotic to a vertical line at 50% exchange of 12 oxygens (a_3 Figure 1).

As the temperature is raised, the rates of exchange of the ' inner oxygens ' increases more rapidly than that of the outer oxygen atoms until at 55 °C the two rates are indistinguishable,[3] * a linear plot being obtained when one assumes 12 kinetically equivalent oxygens [a_1 Figure 1 (v)]. At this temperature $t_{\frac{1}{2}}$ (6 oxygens) = 17 min whence k $(= 6 \times k_{obs}) = 41 \times 10^{-7}$ s^{-1}; $t_{\frac{1}{2}}$ (12 oxygens) = 35·4 min k $(= 12 \times k_{obs}) = 39 \times 10^{-4}$ s^{-1}.

With increase in temperature the rate of aquation of the trisoxalatocobalt ion is observed to increase more rapidly than the rate of outer oxygen exchange (to the extent that only 30% total exchange could be followed at 55 °C). This rapid increase in aquation rate (E_{act} = 30 kcal/mol) is reminiscent of the rapid increase in the rate of inner oxygen exchange (E_{act} = 42 kcal/mol). (E_{act} for outer oxygen exchange is much lower—17 kcal/mol)

The possibility lies open for the exchange of the inner oxygens to occur by a dissociative path, the incorporation of 0—18 labelled carboxyl oxygens being due to the anation of the small amount of the bisoxalatodiaquocobalt(III) anion which is not immediately converted into cobalt(II) products.[8] In fact, by comparison of our data with that of Aggett and Armishaw [8] an ' order of magnitude ' agreement of their rate of anation with our rate of inner oxygen exchange was obtained. At pH 0·8, 17 °C, 25 h of reaction [$t_{\frac{1}{2}}$ $Co(ox)_3^{3-}$ aquation under these conditions] rate of anation = $1{\cdot}3 \times 10^{-7}$ mol l^{-1} s^{-1} per oxygen atom, rate of inner oxygen exchange = $0{\cdot}46 \times 10^{-7}$ mol l^{-1} s^{-1} per oxygen atom.

If any free oxalate [other than that precipitated as

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* Although Broomhead *et al.* have now [4] studied oxygen exchange at 44·40 °C they have not drawn attention to the fact that at this temperature, inner and outer oxygen exchange rates are so similar that the oxygen plot [a_1 Figure 1 (iv)] appears to be almost linear as originally observed.[3]

[5] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' John Wiley, New York and London, 1961.

[6] C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 1964, 4622.

[7] Part VI, J. Aggett and A. L. Odell, *J. Chem. Soc.* (*A*), 1968, 1415.

[8] J. Aggett and R. I. C. Armishaw, *J. Inorg. Nuclear Chem.* 1970, **32**, 1989.

$Co^{II}(ox)$ which is accounted for in the calculations] were removed from solution then the measured rate of inner oxygen exchange would be lower (see Table) and our calculated R_{an} (from data in ref. 8) would be too high, so the two true rates would be closer.

Results for inner and outer oxygen exchange at 17 °C; pH = 0·8

[Complex]	$[H_2C_2O_4]$ (M)	$10^5k/s^{-1}$ (outer oxygen exchange)	$10^7k/s^{-1}$ (inner oxygen exchange)
0·025	0	6·0 ± 0·5	9·6 ± 2
0·05	0·1	5·5 ± 0·5	18 ± 4
0·05	0·2	6·0 ± 0·5	25 ± 5

There are thus three pieces of evidence which suggest that inner oxygen exchange is, in fact, due to incorporation of oxygen-18 into the inner oxygens by anation and not *via* any process similar to carbonyl oxygen exchange. (i) The activation energies for the aquation–anation type reactions are similar to that of inner oxygen exchange and *not* similar to that for outer oxygen exchange.

Outer oxygen exchange $[Co(ox)_3]^{3-}$ E_{act} = 17·2 kcal/mol
Anation = 42 * ± 2 kcal/mol
Inner oxygen exchange = 42 ± 5 kcal/mol
Carbonyl oxygen exchange both in oxalic acid and $[Cr(ox)_3]^{3-}$ = 18 kcal/mol

* Recalculated from data of Aggett and Armishaw.[8]

(ii) The rate of inner oxygen exchange is dependent on free oxalate concentration (as is the anation reaction) whereas the outer oxygen exchange rate is independent of added oxalate (see Table).

(iii) The rates of anation and inner oxygen exchange are approximately equal.

The oxygen exchange of the trisoxalatochromium(III) ion shows there are, in this case, 12 kinetically equivalent oxygen atoms so that the possibility of racemisation of the chromioxalate proceeding *via* a one-ended dissociated species is still viable. The evidence in the case of the cobalt complex now points to such an intermediate being unlikely for the racemisation reaction. The implication for the mechanism of aquation is that the 'first aquation'[7] of the protonated complex to form the diaquo-product proceeds in one reversible step. The observed 'racemisation' of this complex ($k \sim 8 \times 10^{-5}$ s^{-1} in 1M-HCl 25 °C) is, therefore, probably due mainly to aquation ($k_{obs} = 2{\cdot}6 \times 10^{-5}$ s^{-1} in 1M-HCl 25 °C) plus some intramolecular mechanism not involving one-ended dissociation. Gillard *et al.*[9] suggest that $Co(C_2O_4)_3{}^{3-}$, $3\frac{1}{2}H_2O$ in the crystalline state probably contains dechelated oxalate groups, but this is apparently not the case in aqueous solution, at least at 25 °C.

The exchange of the outer oxygen atoms is dependent on acid concentration as shown in Figure 3. These oxygens must be able to exchange while the oxalate group is still bound to the cobalt atom, and the exchange is probably a proton-assisted reaction involving the carbonyl bond and a water molecule.[3] This would agree with the data presented in Figure 3 where the plot, although not linear does show very much more linearity than expected for *A*-1 type acid-catalysed reactions and the reaction can probably be fairly adequately represented as an *A*-2 bimolecular reaction as for the chromioxalate case.

We thank the Research Committee of the New Zealand University Grants Committee for a grant to purchase the Mass Spectrometer.

[1/1143 *Received, 5th July,* 1971]

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[9] R. D. Gillard, S. H. Laurie, and P. R. Mitchell, *J. Chem. Soc.* (*A*), 1969, 3006.