882. *The Reactivity of Co-ordinated Oxalate. Part III.*[1] *Ligand Exchange Reaction Between the Trisoxalatochromium*(III) *Anion and* [^{14}C]*Oxalate.*

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The exchange of [^{14}C]oxalate ions with the trisoxalatochromium(III) anion has been studied. The reaction is much slower than the exchange of solvent oxygen atoms with the same complex. Oxalate-dependent and oxalate-independent paths have been separated experimentally, and the former shown to consist of acid-dependent and acid-independent parts. The oxalate-dependent reaction is a bimolecular substitution. A mechanism involving a " one ended dissociation " of the co-ordinated oxalate group is suggested.

THE chemistry of the metal oxalato-complexes has recently been reviewed.[2] The first investigation of the ligand exchange reaction of the trisoxalatochromium(III) anion, made by Long[3] in a dexterous experiment using carbon-11, established that there was no

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[1] Part II, Bunton, Carter, Llewellyn, Odell, and Yih, preceding Paper.

[2] Krishnamurty and Harris, *Chem. Rev.*, 1961, **61**, 213.

[3] Long, *J. Amer. Chem. Soc.*, 1939, **61**, 570; 1941, **63**, 1353; 1951, **73**, 537.

appreciable exchange during the observable lifetime of the carbon-11. Two groups have reinvestigated this system using carbon-14.[4,5] Both reported complex behaviour in which oxalate-dependent as well as oxalate-independent paths for the exchange reaction were detected. Both groups found the reactions to be acid-catalysed and also to show an acid-independent path. We [5] suggested a mechanism in which the oxalate group suffered a rapidly reversible one-ended dissociation preceding either the rate-determining aquation or oxalate addition steps. Graziano and Harris suggested [4] a similar mechanism:

$$\mathrm{Cr(C_2O_4)_3{}^{3-} + H_2O \rightleftharpoons Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3,H_2O^{3-}} \tag{1}$$

$$\mathrm{Cr(C_2O_4)_3{}^{3-} + H_3O^+ \rightleftharpoons Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3H,H_2O^{2-}} \tag{2}$$

$$\mathrm{Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3,H_2O^{3-} + H_2O \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2{}^- + C_2O_4{}^{2-}} \tag{3}$$

$$\mathrm{Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3H,H_2O^{2-} + H_2O \rightleftharpoons Cr(C_2O_4)_2(H_2O)_2{}^- + HC_2O_4{}^-} \tag{4}$$

$$\mathrm{Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3,H_2O^{3-} + H{*}C_2O_4 \rightleftharpoons Cr(C_2O_4)_2{\cdot}O{\cdot}{*}C_2O_3,H_2O^{3-} + HC_2O_4{}^-} \tag{5}$$

$$\mathrm{Cr(C_2O_4)_2{\cdot}O{\cdot}C_2O_3H,H_2O^{2-} + H{*}C_2O_4 \rightleftharpoons Cr(C_2O_4)_2{\cdot}O{\cdot}{*}C_2O_3H,H_2O^{2-} + HC_2O_4{}^-} \tag{6}$$

This scheme was supported by kinetic data consistent with the following kinetic form for the reactions:

$$\text{Rate} = [\text{complex}]\{k_a + k_b[\text{oxalate}] + k_c[\text{H}^+] + k_d[\text{H}^+][\text{oxalate}]\}$$

and values at 75° were given as follows: $k_a = 1{\cdot}1 \times 10^{-6}$ sec.$^{-1}$; $k_b = 1{\cdot}1 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$; $k_c = 1{\cdot}8 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$; $k_d = 2{\cdot}6 \times 10^{-1}$ l.^{2} mole^{-2} sec.$^{-1}$. These constants were evaluated by best-fit procedures from the kinetic results from the four simultaneous reactions.

We reported [5] a method of suppressing the oxalate-independent reactions by using a high concentration of free oxalate and obtained rather different values for the constants k_b and k_d. We now present these results in detail.

EXPERIMENTAL

Potassium trisoxalatochromium(III) was prepared and analysed as in Part I (Found: Cr, 10·6; $(C_2O_4)^{2-}$, 54·5; H_2O, 11·0. Calc. for $K_3Cr(C_2O_4)_3,3H_2O$: Cr, 10·6; C_2O_4, 54·2; H_2O, 11·1%). [^{14}C]Sodium oxalate was prepared from [^{14}C]sodium formate (supplied by A.E.R.E., Amersham) by heating in an evacuated tube at 400° for 30 min. The product, with 5 g. of sodium oxalate, was dissolved in the minimum of hot water and precipitated by addition of 5 volumes of absolute alcohol.

Exchange Runs.—Solutions of [^{14}C]sodium oxalate and the complex were mixed in a stoppered flask in a thermostat. Samples were removed at time intervals, and free and complexed oxalate were separated as follows. The free oxalate was precipitated with silver nitrate solution and centrifuged. The liquor was then filtered (Whatman No. 42 paper) to remove traces of the filmy precipitate. A solution of hexamminecobalt(III) was added to precipitate the complex and, with dilute solutions of complex, it was found advisable to cool in ice and to scratch the vessel with a glass rod to hasten precipitation. The precipitate was filtered off on a demountable stainless steel funnel, and dried under an infrared lamp, the paper being held flat by a heavy stainless-steel locking ring. The sample was then counted with a Geiger–Müller counter to a standard deviation of 1%. The activity at infinite time was calculated from the concentrations of the reactants, isotope effects being neglected, and the fraction of exchange (F) at each sampling time was calculated.

RESULTS AND DISCUSSION

Results of a preliminary run are in Table 1. The plot of $-\log(1 - F)$ against time [6] is not linear (Fig. 1), reaction apparently slowing down as it proceeds. This might be due

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[4] Graziano and Harris, *J. Phys. Chem.*, 1959, **63**, 330.

[5] Llewellyn and Odell, *Proc. Australian Atomic Energy Symposium*, 1958, **5**, 623.

[6] McKay, *Nature*, 1938, **142**, 997.

TABLE 1.

Exchange of [^{14}C]oxalate with trisoxalatochromium(III) anion at 47°.

[" Complexed " oxalate] = 0·100M. [" Free " oxalate] = 0·0254M.

Time (hr.)	18	91	191	233	304	402	521
$-\log(1-F)$	0·004	0·023	0·040	0·048	0·055	0·066	0·068

to a progressive loss of one of the exchanging species. The trisoxalatochromium(III) anion is known [1,7] to suffer aquation in acid solution in a time comparable with the reaction times discussed here. The product of aquation is *cis*-diaquobisoxalatochromium(III), and this undergoes [7] negligible exchange with oxalate ions under our conditions. The progress of aquation was followed by measuring the optical density at 417 mμ during reaction. The molar extinction coefficient fell from 96·1 to 93·5 after 522 hours; for *cis*-diaquobisoxalatochromium(III) complex it is 68·5, so there was about 9·4% conversion. In the same run, however, the initial rate is about seven times the final rate, so there must operate some other process much more important than aquation.

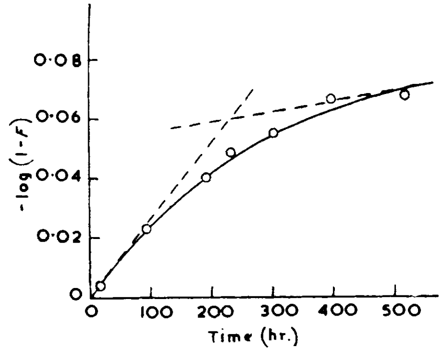

FIG. 1. Exchange of [^{14}C]oxalate with trisoxalatochromium(III) anion.

The pH of the solution changes from 6·6 at zero time to 7·5 after 522 hours, an eight-fold fall in hydrogen-ion concentration. The curvature of the McKay plot is therefore attributed to this change in acidity owing to the reaction:

$$Cr(C_2O_4)_3^{3-} + H^+ + 2H_2O \longrightarrow Cr(C_2O_4)_2,(H_2O)_2^- + HC_2O_4^-$$

Since this reaction is reversible,[8] subsequent exchange runs were done with a high concentration of sodium hydrogen [^{14}C]oxalate. This kept the pH constant at 2·8, measured at 25°, throughout the reaction without introducing extraneous anions, and also provided the high concentration of hydrogen oxalate ions necessary to suppress aquation. Optical densities at 417 mμ remained constant during exchange runs to 1% under these conditions showing effectively complete suppression of aquation reaction. Results of a typical run are in Table 2 and Fig. 2, where the McKay plots are linear.

Rates of the reactions were calculated from the slopes of the McKay plots using the equation: [6]

$$Rt\frac{ab}{a+b} = -\log(1-F)$$

where R = rate of reaction, F = fraction of exchange, a and b are concentrations of " free " and " complexed " oxalate, respectively, and t = time.

Results at different concentrations of the reactants and at two temperatures are in Table 3. The plot of $k_1 = R/[\text{oxalate}]$ against [complex] at pH = 2·8 is (Fig. 3*A*) linear and shows an essentially zero intercept at zero complex concentration. We conclude that

[7] Krishnamurty and Harris, *J. Phys. Chem.*, 1960, **64**, 346.

[8] Hamm and Perkins, *J. Amer. Chem. Soc.*, 1955, **77**, 2083.

TABLE 2.

Exchange of [^{14}C]oxalate with trisoxalatochromium(III) anion at 47°.

[" Free " oxalate] (*a*) = 0·1012M. [" Complexed " oxalate] (*b*) = 0·0252M.

pH 1·8.

Time (hr.)	$-\log(1 - F)$
12·0	0·361
18·5	0·539
24·5	0·688
28·5	0·841
34·0	0·932

$R = 1{\cdot}61 \times 10^{-3}$ mole. l.$^{-1}$ hr.$^{-1}$.

(*a*) = 0·1012; (*b*) = 0·0252; pH 2·3.

Time (hr.)	$-\log(1 - F)$
12·0	0·138
18·5	0·235
24·5	0·310
30·5	0·356
47·25	0·570

$R = 5{\cdot}80 \times 10^{-4}$ mole. l.$^{-1}$ hr.$^{-1}$.

(*a*) = 0·1012; (*b*) = 0·0252; pH 3·0.

Time (hr.)	$-\log(1 - F)$
12·0	0·052
18·5	0·080
24·5	0·121
30·5	0·141
47·25	0·218

$R = 1{\cdot}71 \times 10^{-4}$ mole l.$^{-1}$ hr.$^{-1}$.

(*a*) = 0·1012; (*b*) = 0·0252; pH 3·1.

Time (hr.)	$-\log(1 - F)$
12·0	0·038
18·5	0·060
24·5	0·067
30·5	0·089
47·25	0·133

$R = 1{\cdot}33 \times 10^{-4}$ mole l.$^{-1}$ hr.$^{-1}$.

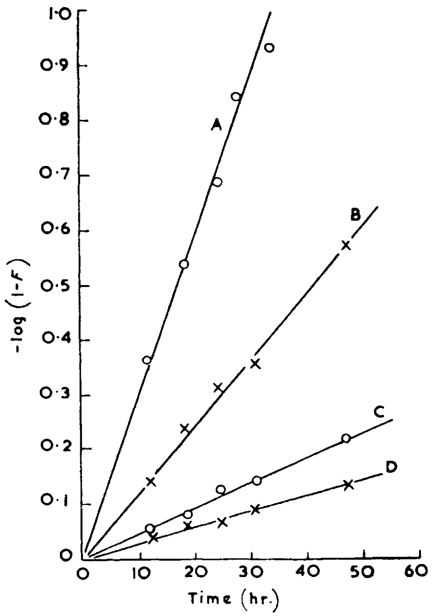

FIG. 2. Exchange of [^{14}C]oxalate with trisoxalatochromium(III) anion.
A, pH 1·8; *B*, pH 2·3; *C*, pH 3·0; *D*, pH 3·1.

the reaction is of first order in complex concentration. Similarly, the plot of $k_1' = R/[\text{complex}]$ against [oxalate] is linear and extrapolates to zero at zero oxalate concentration. This indicates that only oxalate-dependent paths are being observed under these conditions.

Hamm and Perkins [8] have shown that the rate of addition of oxalate ions to the *cis*-diaquobisoxalatochromium(III) anion is independent of the concentration of oxalate ion and this has recently been confirmed.[9] We therefore conclude that the aquation of trisoxalatochromium(III) to form *cis*-diaquobisoxalatochromium(III) and the subsequent

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[9] Odell, unpublished results.

TABLE 3.

Exchange reaction of [^{14}C]oxalate with trisoxalatochromium(III) anion.

Temp.	(*b*)	(*a*)	pH	10^4R (mole l.$^{-1}$ hr.$^{-1}$)
47°	0·0189	0·106	2·8	2·28
47	0·0191	0·101	2·8	2·34
47	0·0254	0·104	2·8	2·69
47	0·0250	0·1006	2·8	2·71
47	0·0125	0·0774	2·8	1·03
47	0·0125	0·0764	2·8	0·979
47	0·0125	0·0497	2·8	0·558
47	0·0125	0·0509	2·8	0·596
47	0·0252	0·1012	1·8	16·10
47	0·0252	0·1012	2·3	5·80
47	0·0252	0·1012	3·0	1·71
47	0·0252	0·1012	3·1	1·33
34·2	0·0129	0·0509	2·8	0·315
34·2	0·0125	0·0759	2·8	0·402
34·2	0·0253	0·1015	2·8	0·932
34·2	0·0188	0·1019	2·8	0·855
34·2	0·0125	0·101	2·8	0·745

addition of oxalate to this latter do not constitute a significant path for the exchange of oxalate in these conditions, the aquation having been effectively suppressed by the high concentration of oxalate ions. This enables us to determine values of the rate constants k_b and k_d without the complications due to aquation and the reverse anation reactions represented by k_a and k_c, as encountered by Graziano and Harris.[4]

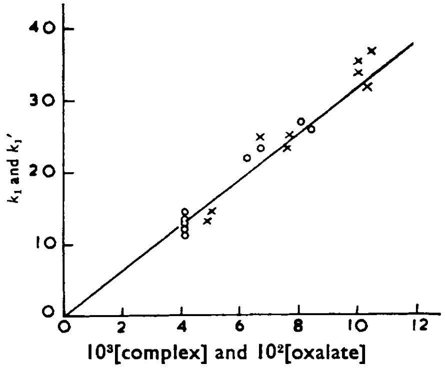


FIG. 3*A*. Dependence of rate of ligand exchange on the concentration of complex and oxalate.

○ k_1 *vs.* [complex] × k_1' *vs.* [oxalate]

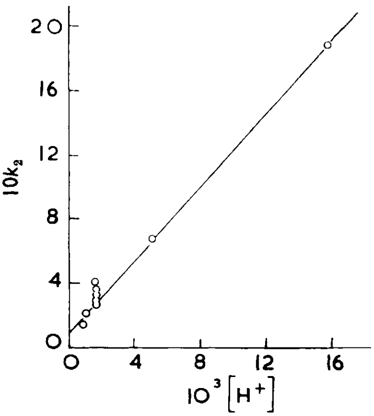


FIG. 3*B*. Dependence of rate of ligand exchange on acid concentration.

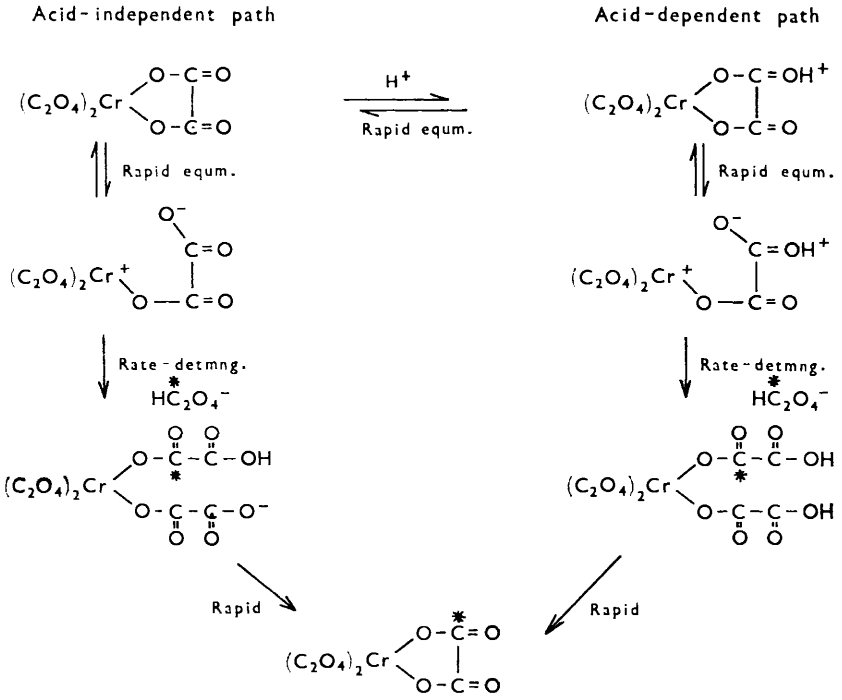
From the plot of the second-order rate constant $k_2 = R/([\text{complex}][\text{oxalate}])$ against $[H^+]$ (Fig. 3*B*), we deduce values for k_b and k_d as follows:

$$R = [\text{complex}](k_b[\text{oxalate}] + k_d[H^+][\text{oxalate}])$$
$$k_b = 2{\cdot}2 \times 10^{-4}\ \text{l. mole}^{-1}\ \text{sec.}^{-1}\ \text{at } 47° \ (1{\cdot}1 \times 10^{-4} \text{ at } 75°)$$
$$k_d = 0{\cdot}331\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}\ \text{at } 47° \ (0{\cdot}26 \text{ at } 75°)$$

These values may be compared with those of Graziano and Harris [4] from data obtained at 75°, shown in parentheses.

Reaction rates were also studied at 34·2° and pH 2·8. While the two constants k_b and k_d could not be obtained from experiments at this one acidity, energy of activation and frequency factor for the combined oxalate-dependent reactions were estimated approximately by using the rate constant k_2: $E(\text{act}) \approx 13{\cdot}1$ kcal./mole; $\log_{10}A \approx 4{\cdot}8$ at 34·2° and pH 2·8. These must be regarded as preliminary estimates only, but the activation energy so obtained appears to be significantly less than that reported by Graziano and Harris [4] for combined oxalate-dependent and oxalate-independent paths, *viz.*, *ca.* 20 kcal. mole^{-1}. The values observed are not inconsistent with the assignment of bimolecular mechanisms for the acid catalysis and acid-independent exchange reactions studied here.

Our observations, in general, support the mechanism suggested by Graziano and Harris [4] but we prefer to formulate the " one ended dissociation " step in such a way as to leave the vacated site on the octahedron unaquated for the reasons discussed in Part II. If this site is vacant, the bimolecular addition of the hydrogen oxalate ion can take place here and it is no longer necessary to invoke a simultaneous bond making and bond breaking process as postulated by Graziano and Harris.[4] We suggest the following mechanism for the oxalate-dependent ligand exchange reactions (overall charges on the complex anions have been omitted for simplicity):



The oxalate-independent reactions can be formulated as aquation and anation reactions discussed in Part II.[1]

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