880.   *The Reactivity of Co-ordinated Oxalate. Part I. Oxygen*-18 *Exchange Studies on Oxalic Acid, the Trisoxalatochromium*(III) *Anion, and the Trisoxalatocobalt*(III) *Anion.*

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The rates of acid-catalysed exchange of oxygen atoms between the solvent water and the trisoxalato-complexes of chromium(III) and cobalt(III) and also oxalic acid have been studied by use of oxygen-18. Carbonyl and carboxyl oxygen atoms have been shown to be kinetically equivalent. The rates of exchange follow the stoicheiometric acidity up to high acid concentrations. Energies of activation are similar for the three solutes. A mechanism involving " one ended dissociation " of the oxalate group is suggested.

EARLY interest in the reactivity of oxalate ions co-ordinated to transition-metal ions was centred about the discussion of the mechanism of racemisation of the trisoxalato-chromium(III) anion. The early conflict of views between Werner,[1] who suggested that one end of an oxalate group momentarily vacated one co-ordination position and then rejoined in a new position, and Thomas [2] who favoured a complete dissociation of an oxalate ion was resolved by Long [3] who showed that [^{11}C]oxalate ion did not exchange with the complex in the time required for complete racemisation. This effectively precludes the " dissociation " hypothesis and leaves the " one-ended dissociation " possibility open.

Reactions of the trisoxalato-complexes of chromium(III) and cobalt(III) in aqueous solution, aquation, oxygen-18 exchange with the solvent, and exchange of isotopically labelled oxalate ions, previously described [4] are in this and the two following Papers reported in detail. These results support the " one ended dissociation " hypothesis.

EXPERIMENTAL

Preparations.—Potassium trisoxalatochromium(III) *trihydrate.* To a solution of potassium oxalate monohydrate (23 g.) and oxalic acid dihydrate (58 g.) in water (800 ml.) were added powdered potassium dichromate (19 g.) in small portions with vigorous stirring. When reaction ceased, the solution was evaporated nearly to dryness and allowed to crystallise. Deep green crystals with a blue irridescence were obtained which were crystallised from aqueous alcohol and then from water, then dried with alcohol and ether (yield 45 g.).

The product was analysed by decomposition by boiling with 10% potassium hydroxide for 10 min., filtering off the precipitated chromic hydroxide, and titrating the filtrate and washings with acidified potassium permanganate. The chromic hydroxide was dissolved in sulphuric acid and oxidised by boiling with excess of potassium bromate, acidified with hydrochloric acid, treated with excess of potassium iodide, and titrated with sodium thiosulphate (Found: Cr, 10·6; C$_2$O$_4$, 54·4; H$_2$O, 11·2. Calc. for K$_3$Cr(C$_2$O$_4$)$_3$,3H$_2$O: Cr, 10·7; C$_2$O$_4$, 54·2; H$_2$O, 11·1%).

Potassium trisoxalatocobalt(III) 3½-*Hydrate.*—To a warm solution of oxalic acid dihydrate (25·2 g.) and potassium oxalate monohydrate (73·7 g.) was slowly added cobaltous carbonate (23·8 g.). When the solution had cooled to 40°, lead dioxide (23·9 g.) was added followed by the slow addition of glacial acetic acid (25 ml.). The mixture was stirred for 3 hr. and filtered. Alcohol (500 ml.) was added and the precipitate filtered off and dried with alcohol and ether. The product was crystallised from water by addition of alcohol and stored in a brown bottle to avoid photolysis (yield 55 g.).

Analysis for oxalate was as described for the chromium complex. The precipitated cobaltic oxide was shaken with potassium iodide and hydrochloric acid and titrated with sodium thio-

[1] Werner, *Ber.*, 1912, **45**, 3061.
[2] Thomas, *J.*, 1921, **119**, 1140; 1922, **121**, 196; 1923, **123**, 2973.
[3] Long, *J. Amer. Chem. Soc.*, 1939, **61**, 570; 1941, **63**, 1353; 1951, **73**, 537.
[4] Llewellyn and Odell, *Proc. Australian Atomic Energy Symp.*, 1958, **5**, 623.

sulphate (Found: Co, 11·66; C_2O_4, 52·2; H_2O, 12·2. Calc. for $K_3Co(C_2O_4)_3,3·5H_2O$: Co, 11·7; C_2O_4, 52·45; H_2O, 12·53%).

Exchange Runs.—The finely powdered oxalates were dissolved in acidified water enriched in oxygen-18 and the mixture immersed in a thermostat. Samples were withdrawn at intervals and the simple or complex oxalate precipitated with the reagent described below. The dried precipitate was pyrolysed by heating either, (*a*) on a graphite block heated to *ca.* 1000° by a radio-frequency furnace in a vacuum system,[5] or (*b*) in an evacuated glass tube to just below the softening point of glass. These two methods were shown to give identical results within experimental error. The carbon dioxide evolved was trapped with liquid nitrogen and the abundance of [^{18}O]carbon dioxide determined in the mass spectrometer.

Oxalic Acid Exchange.—Precipitation was by barium hydroxide in a nitrogen atmosphere. Pyrolysis was by method (*a*). Results of a typical run are in Table 1, the oxygen-18 enrichment value at infinite time being obtained by direct measurement after ten half lives.

TABLE 1.

Exchange of oxalic acid with [^{18}O]water at 79°.

[Oxalic acid] = 0·15M.   pH = 2·587.

Time (min.)	Atom % excess abundance of ^{18}O	$1 - F$	Time (min.)	Atom % excess abundance of ^{18}O	$1 - F$
30	0·027	0·971	352	0·493	0·432
61	0·129	0·851	464	0·583	0·328
127	0·229	0·736	914	0·773	0·109
225	0·362	0·583	∞	0·868	—

$$k_1 = 1·65 \times 10^{-3} \text{ sec.}^{-1}.$$

Log$(1 - F)$ (where F is the fraction of exchange) is plotted against time in Fig. 1; the plot is strictly linear to 89% exchange. The rate of exchange of oxygen atoms (R) is calculated by using a modified [6] McKay [7] equation appropriate to a system in which the concentration of one reactant (water) is large and in which there are four reacting atoms in a molecule of the other reactant:

$$R = 4[\text{oxalate}]0·693/t_{\frac{1}{2}}.$$

First-order rate constants are obtained by dividing this rate by the concentration of oxalic acid used.

Acid dependence of the rate of exchange was studied in hydrochloric acid solutions by the pyrolysis method (*a*); results are in Table 2. Fig. 2 is a plot of the first-order rate constant.

TABLE 2.

Acid dependence of the rate of oxygen-18 exchange of oxalic acid with water.

[Oxalic Acid] (M)	[HCl] (M)	Temp.	$10^4 k_1$ (sec.$^{-1}$)	[Oxalic Acid] (M)	[HCl] (M)	Temp.	$10^4 k_1$ (sec.$^{-1}$)
0·50	0·304	25°	1·76	0·10	2·000	25	15·1
0·50	0·454	25	2·83	0·10	4·000	25	26·1
0·50	0·607	25	3·94	0·10	1·000	44·6	46·1
0·50	0·908	25	5·60				

The rate is proportional (to a good degree of approximation) to the stoicheiometric acidity up to at least 4M-acid. Activation energy and frequency factors for this reaction were estimated approximately from measurements at 25 and 44·6°, the Arrhenius relationship being assumed to hold, whence E (act.) = 18·4 kcal./mole and $\log_{10}A$ = 10·3 for 1M-acid.

Potassium Trisoxalatochromium(III).—The study of the oxygen exchange here is complicated by simultaneous aquation (see Part II). The reagent [(trisethylenediaminecobalt(III))] used to precipitate the complex from the reaction mixture precipitates the trisoxalate uncontaminated by the aquation product, *cis*-diaquobisoxalatochromium(III). Results of a typical run are in Table 3 and $(1 - F)$ is plotted against time in Fig. 3.

[5] Aggett, Bunton, Lewis, Llewellyn, O'Connor, and Odell, *J. Appl. Radiation Isotopes*, 1964, in the press.
[6] Wahl and Bonner, "Radioactivity Applied to Chemistry," Wiley, New York, 1951, p. 11.
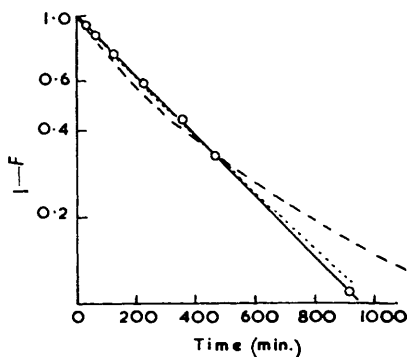[7] McKay, *Nature*, 1938, **142**, 997.

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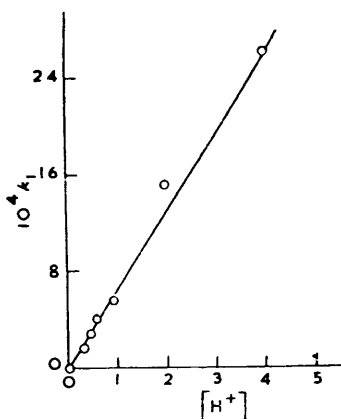FIG. 1. Exchange of oxalic acid with [^{18}O]water.

FIG. 2. Acid dependence of the rate of oxygen-18 exchange of oxalic acid with water.

FIG. 3. Exchange reaction between potassium trisoxalatochromium(III) and [^{18}O]water.

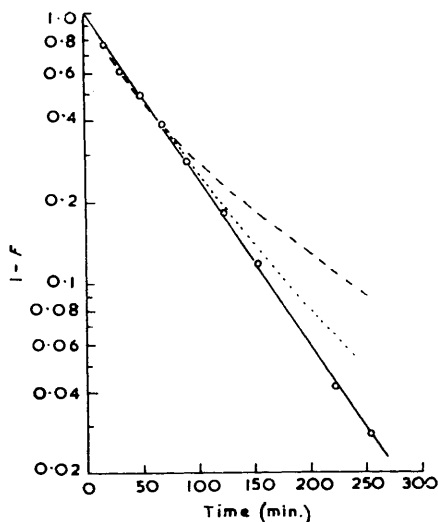TABLE 3.

Exchange reaction between potassium trisoxalatochromium(III) and [^{18}O]water at 25·5°.

[Complex] = 0·10M.   [HCl] = 2·0M.

Time (min.)	Atom % excess abundance of ^{18}O	1 − F	Time (min.)	Atom % excess abundance of ^{18}O	1 − F
17·5	0·164	0·7588	124·0	0·558	0·1794
32·5	0·258	0·6206	154·0	0·601	0·1161
49·0	0·346	0·4911	225·0	0·652	0·0412
69·0	0·420	0·3824	255·0	0·661	0·0279
92·0	0·489	0·2809	∞	0·680	—

$$k_1 = 2·7 \times 10^{-3} \text{ sec.}^{-1}.$$

Non-equivalent Atoms.—The co-ordinated oxalate molecule contains two kinds of oxygen atom, " carbonyl " and " carboxyl," and these might be expected to exchange at different rates. An extension of McKay's equation [8] to cover the case of two atoms, *a* and *b*, exchanging at different rates but not exchanging with each other, is of the form

$$(1 - F) = \tfrac{1}{2}\{\exp - (2R_a t/A) + \exp - (2R_b t/A)\},$$

[8] Wahl and Bonner, ref. 6, p. 13.

where R_a and R_b are the respective rates of exchange of the two kinds of atom, F is the fraction of exchange and A is the total concentration of exchanging atoms. In Fig. 3 the broken curve shows the form McKay's curve would take if $R_a = 2R_1$ and $R_b = R_1/2$, and the dotted curve shows the form expected if $R_a = \sqrt{2}R_1$ and $R_b = R_1/\sqrt{2}$, where $R_1 =$ rate of exchange of one kind of atom $= \frac{1}{2}R$ and $t =$ time. The rates of exchange of the two kinds of oxygen atom are seen to be equal or to differ by a factor less than 2. [Corresponding curves for the case of oxalic acid, where presumably, the " carbonyl " and " carboxyl " oxygen atoms are not kinetically distinct, have been included in Fig. 1 and the McKay plot is linear, departures from linearity being small compared with those expected (dotted curve) if the oxygens were kinetically distinct and reacted at rates differing by a factor of 2.] The kinetic equality of the two kinds of oxygen atom was checked by determining the oxygen abundance of the chromium oxide left after pyrolysing the oxalate complex obtained in a run using water containing 0·775 atom % oxygen-18 by method (*b*); the oxygen-18 abundance was 0·38 atom %, compared with 0·30 atom % obtained by the pyrolysis method.
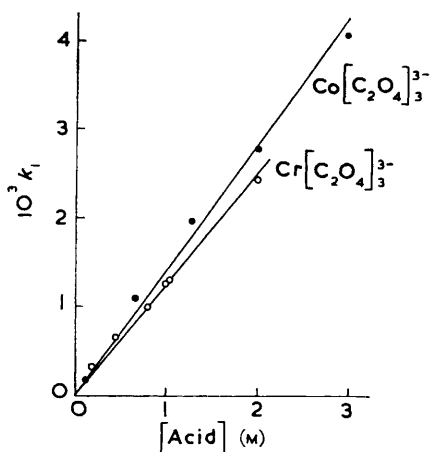

FIG. 4. Acid dependence of the rate of oxygen-18 exchange between the tris-oxalates of chromium(III) and cobalt(III) and water.
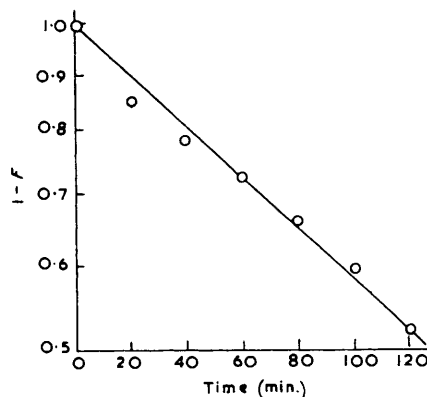
FIG. 5. Exchange reaction between potass-ium trisoxalatocobalt(III) and [¹⁸O]water.

Acid dependence of the rate was studied in hydrochloric acid and in perchloric acid; results are in Table 4 and Fig. 4. The rate is proportional to a good degree of approximation to the stoicheiometric acidity, up to at least 2M-acid.

TABLE 4.

Acid dependence of the rate of oxygen-18 exchange between potassium trisoxalatochromium(III) and solvent water at 25°.

[Complex] (M)	Acid	[Acid] (M)	10^4k_1 (sec.⁻¹)	[Complex] (M)	Acid	[Acid] (M)	10^4k_1 (sec.⁻¹)
0·02	—	—	No exchange	0·02	HCl	0·999	12·75
0·02	HCl	0·199	3·18	0·02	HCl	1·031	13·04
0·02	HCl	0·446	6·53	0·05	HClO₄	2·000	24·18
0·02	HCl	0·796	9·86				

Temperature effects were studied in three runs in 2·0M-perchloric acid at 0, 25, and 44·6°; $10^4 k_1$ was 1·329, 24·18, and 131·3 sec.⁻¹, respectively, whence E (act.) $= 18·01 \pm 0·5$ kcal./mole and $\log_{10}A = 10·64 \pm 0·5$ for 25° and 1M-acid. The Arrhenius plot is shown in Fig. 6.
    The effect of added salts was studied in two experiments in which potassium oxalate (pre-viously equilibrated with oxygen-18 enriched water) and potassium chloride were added. Results are in Table 5.

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TABLE 5.

Effect of added salts on the rate of oxygen-18 exchange between 0·02M-potassium trisoxalatochromium(III) and solvent water at 25°.

[HCl] (M)	0·446	0·446	1·031	1·031
[Salts](M)	—	0·505M-KCl	—	0·201M-$K_2C_2O_4$
$10^4 k_1$ (sec.$^{-1}$)	6·52	5·13	13·03	10·98

Potassium Trisoxalatocobalt(III).—Oxygen-18 exchange of this is also complicated by aquation (see Part II). Both precipitating agents used, trisethylenediaminecobalt(III) and ethanol, precipitate the trisoxalato-complex free from aquation product. Preliminary study showed that identical rates of exchange were obtained by using these two reagents. Typical results are in Table 6 and the McKay plot is in Fig. 5. This run was not continued beyond 50% exchange as the bulk of the material had been converted into the aquation product, and it is not possible to show by this method that the two kinds of oxygen atom are more than approximately

TABLE 6.

Exchange reaction between 0·05M-potassium trisoxalatocobalt(III) and [^{18}O]water at 44·9°.

[Perchloric Acid] = 0·669M.

Time (min.)	Atom % excess abundance of ^{18}O	$1 - F$	Time (min.)	Atom % excess abundance of ^{18}O	$1 - F$
0	0	1	80	0·366	0·654
20	0·160	0·849	100	0·436	0·588
40	0·232	0·781	120	0·512	0·517
60	0·298	0·719	∞	1·060	—

$$k_1 = 1·10 \times 10^{-3} \text{ sec.}^{-1}.$$

kinetically equivalent. Their kinetic equivalence is established, however, by thermal decomposition of the precipitate of formula Co en$_3$ Co(C_2O_4)$_3$ by method (b) to give an oxygen-18 abundance of 0·30 atom % while reduction of the resulting cobalt oxide by carbon gave 0·30 atom % of oxygen-18.

Acid dependence of the rate of exchange was studied in perchloric acid; results are in Table 7 and Fig. 4.

TABLE 7.

Acid dependence of the rate of oxygen-18 exchange between 0·05M-potassium trisoxalatocobalt(III) and solvent water at 44·6°.

[HClO$_4$] (M)	0	0·1184	0·669	1·281	2·00	3·00
$10^4 k_1$ (sec.$^{-1}$)	0	1·76	11·0	19·7	27·85	40·8

The effect of temperature was studied in three runs in 3M-perchloric acid at 0, 25, and 44·6°; $10^5 k$ was 3·595, 63·25, and 408·0 sec.$^{-1}$, respectively, whence E (act) is 18·61 ± 0·5 kcal./mole and $\log_{10} A = 9·96 ± 0·5$ in 1M perchloric acid and 25°. The Arrhenius plot is in Fig. 6.

The effect of added salts was studied at 44·6° in a solution which was 0·05M in complex and 0·669M in perchloric acid. The addition of 0·0952M-cobaltous sulphate lowered the rate constant from 11·0 × 10^{-4} to 8·11 × 10^{-4} sec.$^{-1}$.

Exchange of Labelled Oxalate Ions.—The exchange of carbon-13 labelled oxalate ions with the trisoxalatochromium(III) anion was studied in acid solution. Again, this exchange reaction is complicated by simultaneous aquation. The trisoxalate was precipitated by adding 4 vol. of absolute alcohol to the reaction mixture. The precipitate was redissolved in water and re-precipitated with alcohol. This procedure gave a sample free from aquation products. Carbon dioxide for mass-spectrometric carbon-13 determination was liberated with acidified potassium permanganate (Table 8). There is some scatter in these results but clearly there is very little oxalate ion exchange in 900 min. in 1M-acid. A more detailed study of the exchange of carbon-labelled oxalate ions is reported in Part III.
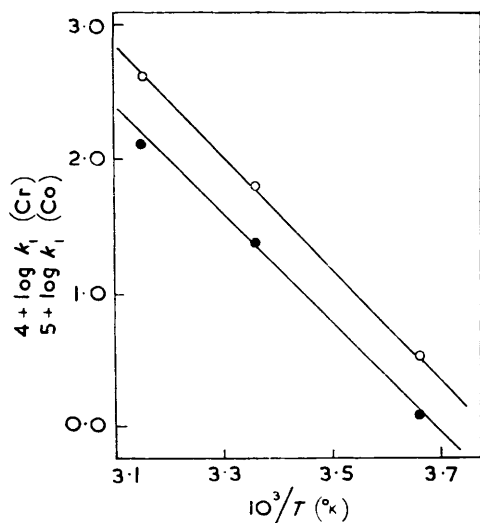
Fig. 6.   Effect of temperature on the rate of exchange reactions of potassium trisoxalatochromium(III) and potassium trisoxalatocobalt(III) with [^{18}O]water.

o Co; ● Cr.

TABLE 8.

Exchange of [^{13}C]oxalate ions with potassium trisoxalatochromium(III).

[" Complexed " oxalate] = 0·0594M.   [" Free " oxalate] = 0·356M.   [HCl] = 1·02M.

Time (min.)	Atom % excess abundance of ^{13}C [*]	1 − F	Time (min.)	Atom % excess abundance of ^{13}C [*]	1 − F
5	0·002	0·995	125	0·028	0·939
36	0·018	0·956	156	0·022	0·952
65	0·088	0·810	183	0·036	0·922
95	0·020	0·957	943	0·086	0·810

[*] Control (no complex), 1·230.   Calc. for complete exchange, 0·461.

DISCUSSION

The rate of acid-catalysed oxygen-18 exchange between oxalic acid and solvent water has been shown to be accurately proportional to the stoicheiometric acidity up to at least 4M-acid.   According to the Hammett–Zucker hypothesis [9] this implies an *A*2 bimolecular mechanism with a water molecule in the transition state.

Accordingly we suggest the following mechanism for this reaction which is similar to that for the acid-catalysed hydrolysis of carboxylic esters.
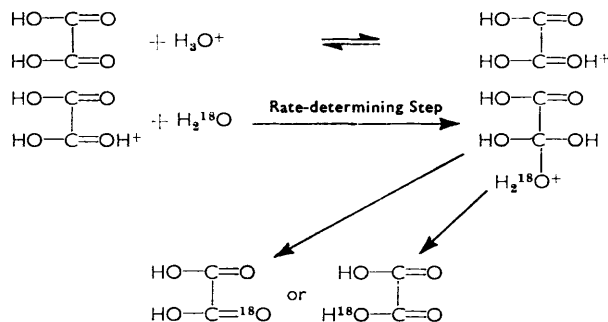

The rates of acid-catalysed oxygen-18 exchange of the trisoxalato-complexes of chromium(III) and cobalt(III) with solvent water are proportional to the stoicheiometric

[9] Zucker and Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

acidity up to 2M and 3M acid, respectively. The two kinds of oxygen atom in these complexes are kinetically equivalent within narrow limits. Activation energies for the exchange reactions are very similar for the chromium complex, the cobalt complex, and for oxalic acid, being 18·0, 18·6, and 18·4 kcal./mole, respectively, while the frequency factors are also similar: $\log_{10} A = 10\cdot35$, 10·64, and 9·96, respectively. In the aquation reaction, on the other hand, the change of central metal atom from chromium to cobalt is accompanied by a change in activation energy of *ca.* 6 kcal./mole (Part II).

These considerations lead us to the view that the oxygen-18 exchange of these complexes takes place by a mechanism similar to that found in the corresponding reaction of oxalic acid. This we represent as a rapid protonation of the carbonyl oxygen atom followed by the rate-determining addition of a water molecule across the carbonyl double bond. In order to account for the enrichment of all twelve oxygen atoms in the complex, and for the fact that carbonyl and carboxyl oxygen atoms are equivalent, however, it is necessary to suppose that some interchange of these two kinds of atom must occur at a rate which is fast compared with the rate-determining addition of water. Complete dissociation of an oxalate molecule would allow such an interchange, but this possibility has been eliminated by the negative results of oxalate-ion exchange reactions in neutral solution [3] and by the very slow exchange reaction in acids referred to above. " One ended dissociation," as suggested by Werner, accounts for the observed facts, but we now suggest that this process is rapid.

The similarities of the activation energies for the reactions of chromium and cobalt complexes and oxalic acid suggest that the rate-determining step occurs at a point remote from the metal atom, and we propose the following mechanism:
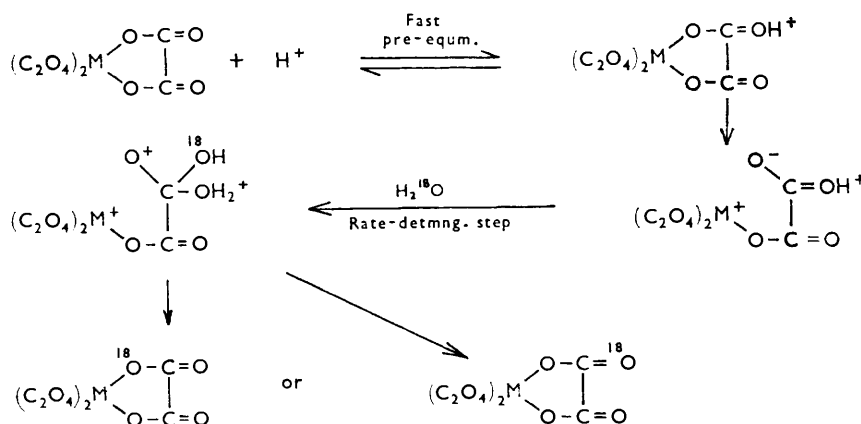
This model implies that the oxalate rings are rapidly opening and closing at one end at a time so that the trisoxalato-complex anion must be visualised as an " oscillating " ion when dissolved in aqueous acids. Recent work by Mason [10] on the trisoxalatocobalt(III) anion indicates that the standing concentration of one-end dissociated molecules is not small.

In the above scheme the position vacated by the dissociating end of the oxalato-group has been left unaquated. The justification for this is the observation by Hamm and Perkins [11] that the anation of the diaquobisoxalatochromium(III) anion by oxalate ion is slow, the rate being independent of the concentration of the oxalate ion. These authors infer that the breaking of the chromium–water bond in this molecule is slow, and since the " one-ended dissociation " process postulated above must be rapid, we suggest that the

[10] Mason and McCaffery, *Proc. Chem. Soc.,* 1962, 388.
[11] Hamm and Perkins, *J. Amer. Chem. Soc.,* 1955, **77,** 2083.

vacated position remain vacant, or that any solvating molecule be loosely bound rather than co-ordinated.

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