881. *The Reactivity of Co-ordinated Oxalate. Part II.*[1] *Acid-catalysed Aquation Reactions of the Trisoxalatochromium*(III) *Anion and the Trisoxalatocobalt*(III) *Anion.*

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The rates of acid-catalysed aquation of the trisoxalato-complexes of chromium(III) and cobalt(III) have been studied in solutions of high acid concentration and the apparent order of the reaction with respect to hydrogen ion concentration shown to increase from approximately unity at 1M-acid to 3·5 and 9·0 for the chromium and cobalt complexes respectively in solutions of high acid concentration. The plots of the logarithm of the first order rate constant against the Hammett acidity function $-H_0$ are linear with slopes of 1·0 and approximately 0·75, respectively. A mechanism for the aquation is suggested.

In a preliminary report[2] on the kinetics of the acid-catalysed aquation of the trisoxalato-complexes of chromium(III) and cobalt(III), the chromium complex was shown to aquate with the formation of the *cis*-diaquobisoxalatochromium(III) anion, while the cobalt complex did not give any detectable intermediate product but aquated to a hexa-aquo-ion. Reaction rates were studied over acid concentrations 1—3·5M for the chromium and 1—10M for the cobalt complexes. The rates follow the Hammett acidity function $-H_0$.

A study[3] of the acid-catalysed aquation of the trisoxalatochromium(III) anion over a restricted range of acid concentration has been reported, and a mechanism involving one proton at low acid concentrations and two protons at higher acid concentrations proposed.

The chemistry of the oxalato-complexes was later reviewed[4] but the work[2] in the more concentrated acids was omitted. We now present these results in detail.

EXPERIMENTAL

Preparations and analyses of the trisoxalato-complexes were as in Part I.[1] Potassium diaquobisoxalatochromium(III) was prepared by a standard method.[5]

Rates of aquation were studied as follows. 50 ml. of aqueous perchloric acid at 25° were poured on 1·231 g. of $K_3Cr(C_2O_4)_3,3H_2O$ crystals, or 1·271 g. of $K_3Co(C_2O_4)_3,3\cdot5H_2O$ crystals in a stoppered flask at 25°, and the mixture shaken. White potassium perchlorate settled out. Samples (2 ml.) were removed at intervals and diluted with 100 ml. of water (changes in optical density were shown to be slow at this dilution) and the optical density d_t measured using the prominent peaks at 416 or 420 mμ for the chromium and cobalt complexes, respectively.

Results.—(1) *Potassium trisoxalatochromium*(III). Optical density at 416 mμ at the time of

[1] Part I, Bunton, Carter, Llewellyn, O'Connor, Odell, and Yih, preceding Paper.
[2] Llewellyn and Odell, *Proc. Australian Atomic Energy Symposium*, 1958, **5**, 623.
[3] Krishnamurty and Harris, *J. Phys. Chem.*, 1960, **64**, 346.
[4] Krishnamurty and Harris, *Chem. Rev.*, 1961, **61**, 213.
[5] King, "Inorganic Preparations," Murby, 1936, p. 111.

View Online

[1964] *The Reactivity of Co-ordinated Oxalate. Part II.* 4623

mixing (d_0) and after many hours (d_∞) was measured in solutions of the trisoxalato-complex and of the bisoxalatodiaquo-complex in 1M-perchloric acid, with and without added oxalic acid (Table 1). The results indicate (a) that the primary aquation product is the *cis*-diaquobisoxalato-chromium(III) species and (b) that aquation is reversible, the same equilibrium position being reached from either the trisoxalato-complex or the di-aquo-complex.

TABLE 1.

Equilibrium study of the aquation of the trisoxalatochromium(III) anion (A) and of the anation of *cis*-diaquobisoxalatochromium(III) anion B at 44·6° in 1M-perchloric acid.

[A]	[B]	[$H_2C_2O_4$]	d_0	d_∞
0·05M	0	0	0·746	0·527
0·05M	0	1M	0·746	0·601
0	0·05M	1M	0·527	0·597

TABLE 2.

Aquation of the trisoxalatochromium(III) anion.

[$HClO_4$] = 4M. [Complex] = 0·05M. Temp. = 25°.

Time (min.)	d_t	d_∞	$2 + \log(d_t - d_\infty)$	Time (min.)	d_t	d_∞	$2 + \log(d_t - d_\infty)$
0	0·960	0·725	1·371	43·5	0·724	0·710	0·146
5	0·895	0·723	1·236	50·5	0·720	0·709	0·042
12	0·836	0·720	1·064	57	0·709	0·706	
18	0·790	0·718	0·857	63	0·710	0·703	
24·5	0·770	0·716	0·732	72·5	0·704	0·700	
30·5	0·750	0·714	0·556	122	0·680	—	
36·5	0·739	0·712	0·432	160	0·670	—	

TABLE 3.

Effects of acids on the rate of aquation of trisoxalatochromium(III) anion.

Time (min.)	[H^+] (M)	$-H_0$	$10^4 k_1$ (sec.$^{-1}$)	Time (min.)	[H^+] (M)	$-H_0$	$10^4 k_1$ (sec.$^{-1}$)
	HCl at 44·41°				$HClO_4$ at 25°		
1	0·0471	—	0·162	16	1·00	0·22	0·354
2	0·696	—	0·227	17	1·50	0·53	0·938
3	0·0941	—	0·305	18	2·00	0·78	1·727
4	0·1390	—	0·491	19	3·00	1·23	4·700
5	0·1883	—	0·607	20	3·50	1·47	8·550
6	0·1883	—	0·610				
7	0·155	—	0·417		$HClO_4$ at 44·46°		
8	0·291	—	0·798	21	1·00	—	3·84
9	0·406	—	1·135	22	1·0 *	—	11·32
10	0·581	—	1·783	23	3·0	—	69·20
11	0·782	0·03	2·550				
12	0·992	0·20	3·433		$HClO_4$ at 0°		
13	1·499	0·48	7·433	24	3·0	—	0·1402
14	1·743	0·60	9·333				
15	2·19	0·76	12·750		* 98% D_2O.		

TABLE 4.

Aquation of the trisoxalatocobalt(III) anion.

[$HClO_4$] = 2·73M. [Complex] = 0·05M. Temp. 44·6°.

Time (min.)	d_t	$2 + \log(d_t)$	Time (min.)	d_t	$2 + \log(d_t)$
0	0·548	1·738	4	0·155	1·190
1	0·408	1·610	5	0·115	1·061
2	0·293	1·467	6	0·083	0·949
3	0·216	1·334	∞	0·0	—

The rate of aquation was studied by the method outlined above. Results of a typical run are in Table 2 and Fig. 1. The plot of d_t against time is asymptotic, not to the abcissa, but to a line such as the dashed line in the Figure. This behaviour is ascribed to a slow secondary aquation of the *cis*-diaquobisoxalatochromium(III) anion. In conformity with this, the plot of $\log_{10}(d_t - d_{160\ \text{min.}})$ is (Fig. 1) non-linear. We have corrected for this secondary aquation by reading d_∞ values for the primary aquation from the dashed line (Fig. 1). These values

TABLE 5.

Effect of acids on the rate of aquation of the trisoxalatocobalt(III) anion.

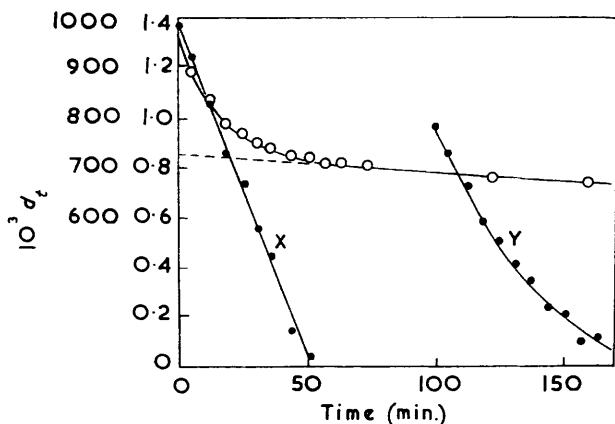| Time (min.)	[H+] (M)	$-H_0$	$10^4 k_1$ (sec.$^{-1}$)	Time (min.)	[H+] (M)	$-H_0$	$10^4 k_1$ (sec.$^{-1}$)
		HClO$_4$ at 25°				H$_2$SO$_4$ at 25°	
1	0	—	Very slow	21	1·00	0·26	0·3385
2	1·00	0·22	0·478	22	2·00	0·84	0·691
3	2·00	0·78	1·26	23	3·00	1·38	1·422
4	3·00·	1·23	3·04	24	4·00	1·85	3·04
5	4·00	1·72	7·95	25	6·00	2·76	14·73
6	5·00	2·23	20·00	26	8·00	3·87	95·80
7	5·46	2·49	34·15				
8	6·00	2·84	65·00			HClO$_4$ at 44·6°	
9	6·50	3·22	108·70	27	1·07	0·27	10·21
10	7·00	3·61	173·30	28	1·45	0·50	17·75
				29	1·97	0·76	29·25
		HCl at 25°		30	2·73	1·11	52·10
11	1·00	0·20	0·259	31	3·38	1·42	92·60
12	2·00	0·69	0·680	32	3·93	1·68	177·6
13	3·00	1·05	1·192	33	4·72	2·08	275·0
14	4·00	1·40	2·39	34	1·00	—	9·56 *
15	5·00	1·76	4·57	35	1·00 †	—	19·6
16	6·00	2·12	9·05				
17	7·00	2·56	17·54				
18	8·00	3·00	32·70		* Calc. from 27.		
19	9·00	3·39	40·80		† 98% D$_2$O.		
20	10·00	3·68	73·20				

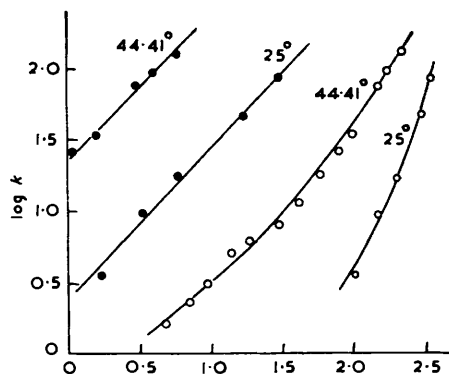FIG. 1. Rate of aquation of the trisoxalatochromium(III) anion.

X log $(d_t - d_\infty)$; Y log $(d_t - d_{160\ min.})$.

FIG. 2. Acid dependence of the rate of aquation of the trisoxalatochromium(III) anion.

○ $2 + \log$ [H+]; ● $-H_0$.

at various times are included in Table 2 under the heading d_∞. The plot of $\log_{10} (d_\infty - d_t)$ is linear, and first-order rate constants were obtained from its slope using the expression

$$k_1 = 2·303/t \log_{10} \frac{(d_0 - d_\infty)}{(d_t - d_\infty)}$$

The values of k_1 at various acidities and at two temperatures are in Table 3 together with the values of the Hammett acidity function $-H_0$ at 25° for solutions [6] over 1M in acid. The plot of $\log k_1$ against $\log$ (stoicheiometric acidity) in Fig. 2 is curved, its slope increasing from *ca.* 0·9 in solutions of low acidity to *ca.* 3·5 in highly acid solutions. The plot of $\log k_1$ against $-H_0$ for the perchloric acid solutions at 25° is linear and has unit slope (Fig. 2). The corresponding

[6] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

plot for the hydrochloric acid solutions is of little significance since k_1 was measured at 44·41° while the $-H_0$ values are for solutions at 25°, the values at 44·41° being unavailable.

An acceleration of the rate by a factor of 2·95 is seen (runs 21 and 22) when the solvent is changed from water to deuterium oxide.

The effect of temperature was studied in 3M-acid in three runs (19, 23, 24) and a linear Arrhenius plot (Fig. 4) obtained whence $E(\text{act.}) = 24\cdot4 \pm 0\cdot2$ kcal./mole. The frequency factor was calculated for 25° and 1M-perchloric acid (run 16) whence $\log_{10} A = 13\cdot5 \pm 0\cdot5$. These data agree tolerably well with those of Krishnamurty and Harris.[3]

TABLE 6.

Effect of temperature on the rate of aquation of the trisoxalatocobalt(III) anion.

[Complex] = 0·05M-$K_3Co(C_2O_4)_3,3\frac{1}{2}H_2O$. [Acid] = 3·93M-$HClO_4$.

Temp.	0°	25°	44·6°
10^6k_1 (sec.$^{-1}$)	8·12	775·0	17,760

(2) *Potassium trisoxalatocobalt*(III). Results of a typical run are in Table 4. There is no evidence of partial aquation as in the case of the chromium complex, the optical density at 420 mμ falling steadily to zero. The effect of varying the acid concentration was studied in
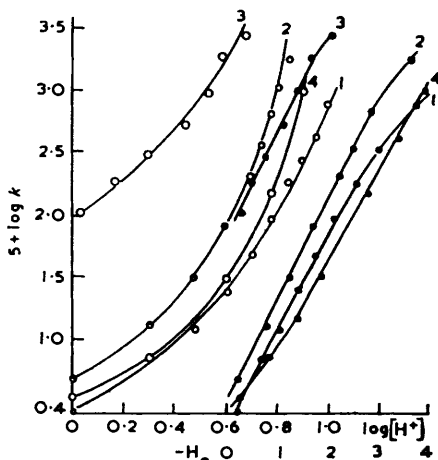

FIG. 3. Effect of acids on rate of aquation of the trisoxalatocobalt(III) anion.

1. Hydrochloric acid at 25°.
2. Perchloric acid at 25°.
3. Perchloric acid at 44·6°.
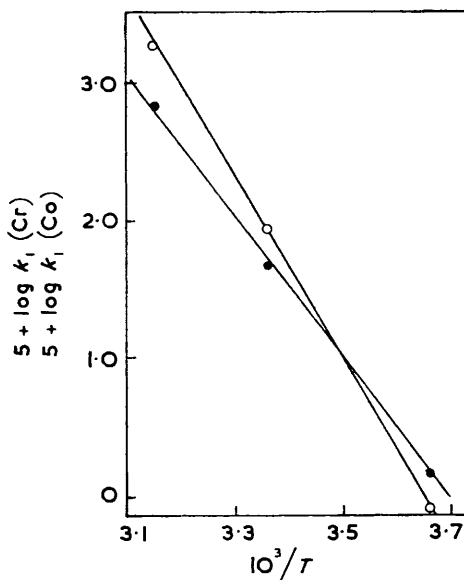4. Sulphuric acid at 25°.

○ log [H$^+$]; ● $-H_0$

FIG. 4. Effect of temperature on the rate of aquation of the trisoxalatochromium(III) anion (●) and the trisoxalatocobalt(III) anion (○).

perchloric acid, hydrochloric acid, and sulphuric acid solutions at 25° and in perchloric acid at 44·6°. Results are in Table 5 and Fig. 3; the slope of the plot of log k_1 against log (stoicheiometric acidity) increases in the case of perchloric acid, from 1·07 at 1M-acid to 9·4 at 7M-acid, while the plot of log k_1 against $-H_0$ is linear with slopes varying from 0·71 to 0·89 for the various acids.

An acceleration of the rate by a factor of 2·03 is seen when the solvent is changed from water to deuterium oxide.

Rates of aquation were determined at three temperatures in 3·93M-perchloric acid (Table 6). From the slope of the Arrhenius plot (Fig. 4) $E(\text{act.}) = 30\cdot35 \pm 0\cdot2$ kcal./mole and $\log_{10} A = 18\cdot0 \pm 0\cdot5$ at 25° in 1M-$HClO_4$.

View Online

4626 *The Reactivity of Co-ordinated Oxalate. Part II.*

DISCUSSION

While the rates of aquation of the trisoxalato-complexes of chromium(III) and cobalt(III) show approximately first-order dependence on acid concentration at low acidities, as the acid concentration is raised the order of the dependence increases in agreement with the observations of Krishnamurty and Harris.[3] The order of the dependence does not tend to two, however, as these authors claim, but continues to increase smoothly up to 3·5 and to approximately 9 respectively for the two complexes. This type of behaviour is not uncommon in acid-catalysed reactions of organic compounds.[7] For an *A*1 unimolecular acid-catalysed hydrolysis of an uncharged species in which a water molecule is not involved in the transition state, Hammett has suggested [8] that the rate should depend linearly on the function h_0, that is that the plot of log k_1 against $-H_0$ should be linear and have unit slope. This behaviour is observed in many acid-catalysed hydrolyses of neutral bases and slopes of 0·8 to 1·2 have been found.[7] The condition that must hold with changing acid concentration is $f_S/f_{SH^+} = f_B/f_{BH^+}$, where f_i represents the activity coefficient of the species i, S is the uncharged substrate, SH$^+$ is a protonated reaction intermediate of approximately the same configuration as the transition state, B is the uncharged indicator base used to measure H_0, and BH$^+$ is its conjugate acid.

The use of Hammett acidity functions has been extended to reactions of charged bases, and functions H_+ and H_- have been defined for singly charged cationic and anionic bases respectively. These functions are measured by use of indicators having appropriate charges. In seeking to extend the use of these functions further to the case of acid-catalysed aquation reactions of the triple negative trisoxalates of chromium(III) and cobalt(III), one faces the difficulty of choosing an indicator of the type B^{3-}. An alternative approach to the problem is to enquire whether H_+ and H_- vary in a parallel manner to H_0, and if so to hypothesise a similar behaviour for H_{3-}, the Hammett function for a triple negative base.

If $f_{S^{3-}}/f_{SH^{2-}} = f_B/f_{BH^+}$ over the range of acid concentration used, then we would expect a linear plot of log k_1 against $-H_0$ with unit slope for an *A*1 reaction.

Coryell and Fix [9] noted a constant difference of 0·8 of a log unit between H_0 and H_- in the range 4—6M-sulphuric acid, and also a close parallelism between H_0 and the Michaelis [10] acidity function G measured up to 11M-sulphuric acid for the uptake of up to three protons. In pure sulphuric acid, where $-H_0$ is 10·6 the difference between H_+ and H_0 has been shown [11] to be only 0·28 log unit. Bonner and Lockhart [12] also found experimentally that a close parallel existed between H_+ and H_0 for solutions of sulphuric acid. Hence it appears that the extension of the use of H_0 as a measure of the protonating power of acid solutions towards charged bases might be permissible. The linear graph, with essentially unit slope, obtained for the Hammett plot of the aquation reactions studied here lends support to the notion that the functions H_0 and H_{3-} show parallel behaviour. The slopes (0·7—0·8) found for the cobalt complex, while somewhat lower than the unit slope expected, are comparable with those found for acid catalysed reactions of many neutral organic bases, and so do not necessarily invalidate these conclusions.

The application of the Hammett acidity function H_0, extended to include reactions of triply charged bases, explains the very high order of dependence of the rates of aquation on acid concentration, and removes the necessity for postulating that more than one proton per molecule of complex is involved in the protonation equilibrium preceding the rate-determining step.

[7] Long and Paul, *Chem. Rev.*, 1957, **57**, 935.
[8] Hammett and Paul, *J. Amer. Chem. Soc.*, 1934, **56**, 830.
[9] Coryell and Fix, *J. Inorg. Nuclear Chem.*, 1955, **1**, 119.
[10] Michaelis, *J. Amer. Chem. Soc.*, 1942, **64**, 1861.
[11] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[12] Bonner and Lockhart, *J.*, 1957, 364.

The accelerations observed in deuterium oxide indicate [13] that there are, in fact, such rapidly established pre-equilibria involving proton addition.

The difference in activation energies of some 6 kcal./mole for the aquation of the chromium and cobalt complexes, indicates that the rate-determining step involves the metal atom (cf. activation energies for oxygen-18 exchange reactions of the same complexes, 18·0 and 18·6 kcal./mole, respectively [1]), while the dependence of the rates upon the Hammett acidity requires [7] that the transition state be similar to the protonated complex, that is, that it does not contain a water molecule.
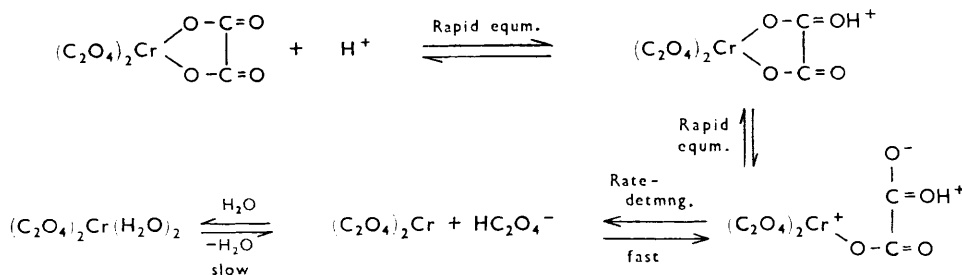
Hamm and Perkins showed [14] and we confirmed [15] that the rate of anation of *cis*-diaquo-bisoxalatochromium(III) is independent of the concentration of the oxalate ion.

In view of these facts, and the considerations in Part I,[1] we propose the above aquation mechanism for the acid catalysed aquatisation of the trisoxalatochromium(III) anion, and a similar mechanism for the corresponding complex of cobalt(III).

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[13] Wiberg, *Chem. Rev.*, 1955, **55**, 713.
[14] Hamm and Perkins, *J. Amer. Chem. Soc.*, 1955, **77**, 2083.
[15] Odell, unpublished results.