Reactivity of Co-ordinated Oxalate. Part IX.[1] The Acid-catalysed Racemisation of Potassium Trisoxalatochromium(III)

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The rate of racemisation of the trisoxalatochromium(III) anion shows a very high order of dependence on acid concentration. We present data for catalysis of the reaction by $HClO_4$, HCl, and H_2SO_4. An *A*-1 mechanism for the racemisation is proposed.

A preliminary study on the acid-catalysed racemisation was carried out by Beese and Johnson.[2] Similar studies were carried out by Yih, Seaton, and Kernohan,[3] but the range of acid concentrations studied was not sufficiently wide for a pattern of dependence to emerge. The data they present have now been extended over a wider range of acids and of concentrations.

EXPERIMENTAL

Preparation and analysis of the complex $K_3Cr(C_2O_4)_3$,$3H_2O$ were as in Part I.[4] Resolution was achieved by way of the strychnine salt.[5]

Optical rotations were measured with a Shimadzu Q.R. 50 spectrophotometer with a polarimeter attachment at a wavelength of 494 nm for slower runs while kinetic runs with half lives of less than 3 min were followed using a JASCO o.r.d./u.v.-5 recording spectropolarimeter. This recording instrument was also used for some slower runs and gave

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[1] Part VIII, preceding paper.

[2] N. W. Beese and C. H. Johnson, *Trans. Faraday Soc.*, 1935, **31**, 1632.

[3] (*a*) S. Y. Yih, Thesis, University of London, 1958; (*b*) F. B. Seaton, Thesis, University of Auckland, 1964; (*c*) J. A. Kernohan, Thesis, University of Auckland, 1965.

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

[5] A. Werner, *Ber.*, 1914, **47**, 1954.

comparable results to those obtained on the manual instrument.

Results of a typical run are shown in Figure 1.

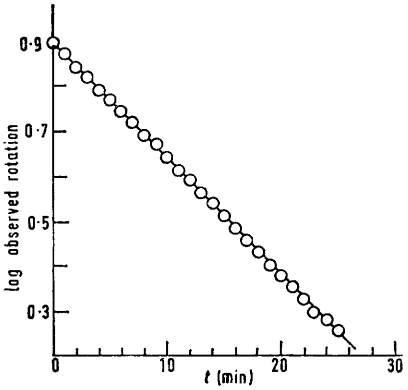


FIGURE 1 First-order plot for the racemisation of $Cr(ox)_3^{3-}$: $[K_3Cr(ox)_3] = 2{\cdot}38 \times 10^{-3}$M, [HCl] = 1·015M, temp. = 0 °C

A plot of the logarithm of the rotation against time was linear, and, from the slope the first-order rate constant was obtained.

Observations in the high acid region were limited by the rate of reaction, which eventually became too rapid to follow with the recording instrument. Standard deviation for k in the region where $[H^+] > 6$M could be as high as ±10%.

RESULTS AND DISCUSSION

The behaviour of potassium trisoxalatochromium(III) was essentially the same in solutions of $HClO_4$, H_2SO_4, and HCl, with small variations due to particular properties of the acids.

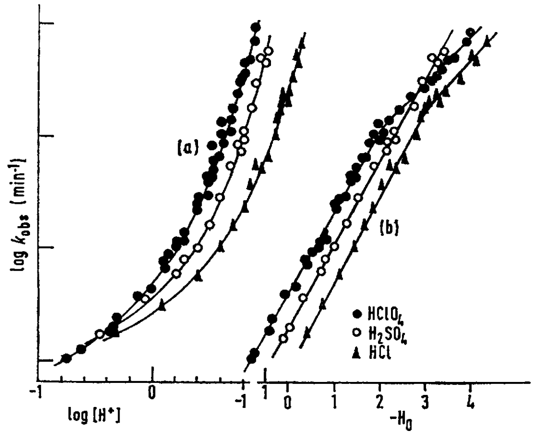


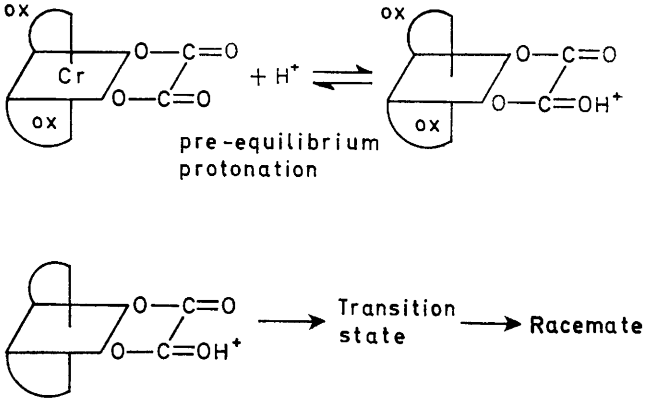
FIGURE 2 Effect of acids on rate of racemisation of the trisoxalatochromium(III) anion. Plots (a) log k_{obs} against log $[H^+]$; plots (b) log k_{obs} against $-H_0$.

For perchloric acid use the log $[H^+]$ and $-H_0$ scales as shown. For H_2SO_4 subtract 0·2 from log $[H^+]$ and 0·5 from $-H_0$. For HCl subtract 0·4 from log $[H^+]$ and 1·0 from $-H_0$

Our results are presented in Figure 2. All complex concentrations are $2{\cdot}4 \times 10^{-3}$M and the temperature is 0·1 °C throughout.

Racemisation in the pH region 4—7 was found to be slow[6] but with a pH below 3 a marked increase in the rate of racemisation with increase in acid concentration was observed. It can be seen (Figure 2) that the rate of racemisation increases at a rate greater than the stoicheiometric acidity. This was observed in the acid-catalysed racemisation of $Rh(ox)_3^{3-}$ (ref. 7) (where ox = C_2O_4) and in the aquation of both $Cr(ox)_3^{3-}$ and $Co(ox)_3^{3-}$.[8]

This type of behaviour, with a high order of dependence on $[H^+]$ is not uncommon for acid-catalysed reactions, and, as with the results for the aquation of $Cr(ox)_3^{3-}$ and $Co(ox)_3^{3-}$ (ref. 8) the results for the racemisation reactions have been plotted against the Hammett acidity function, H_0.[8–10] The plots of log k_{obs} against log $[H^+]$ show smooth curvature from a slope of zero at pH 4 to slopes of 4·3, 4·1, and 4·2 for $HClO_4$, H_2SO_4, and HCl respectively at high acid concentrations. The Hammett plots, however, are almost linear with slopes (at least over the region where $[H^+] < 4{\cdot}5$M or $-H_0 < 2{\cdot}0$ for $HClO_4$ and HCl) not very far removed from unity (0·73). According to Hammett[11] such a plot suggests an A-1 unimolecular mechanism which does not involve a water molecule in the transition state, *e.g.*



The change in slope in the Hammett plots for HCl and $HClO_4$ is probably real rather than a result of the larger experimental error at high acidity, and can also be observed in the results presented[8] for acid-catalysed aquation of $Cr(ox)_3^{3-}$. The change in slope appears at the same acid concentration in all four cases (two aquation, two racemisation) and is probably traceable to the use of unsuitable acidity functions in this region (see discussion in ref. 8). Alternatively, it could be due to some change in mechanism caused by the dehydration of the reaction solution or by some change in proportion of inversion proceeding *via* one route to that proceeding

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[6] D. Shooter, personal communication.

[7] Part IV, A. L. Odell, R. W. Olliff, and F. B. Seaton, *J. Chem. Soc.*, 1965, 2280.

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

[9] F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 12.

[10] K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408.

[11] L. P. Hammett and L. Zucker, *J. Amer. Chem. Soc.*, 1934, **56**, 830.

by some alternative route. Alternative acidity function treatments[12,13] of our data were attempted, but gave no linear dependences and are considered not suitable for the chromioxalate system.

While it now appears that a slow rate-determining racemisation of the protonated complex proceeds with no intervention of a water molecule, the nature of the transition state remains a matter for speculation.

If, however, the oxygen exchange of $Cr(ox)_3^{3-}$ with solvent water is considered,[4] we find that at 25 °C in 1M-$HClO_4$ $k_{racemisation} = 1{\cdot}38 \times 10^{-2}\ s^{-1}$ while $k_{O^{18}\ exchange} = 1{\cdot}26 \times 10^{-3}\ s^{-1}$, *i.e.* racemisation is *ca.* 10 times as fast as oxygen exchange. All 12 oxygens of $Cr(ox)_3^{3-}$ are kinetically equivalent which means ring opening and closing must be fast compared with oxygen exchange or a curved McKay plot for exchange would be observed.[4] In fact, the ring opening and closing might well be fast enough to provide a route for racemisation with the formation of an intermediate which could have either one or two oxalate groups in a 'one-end dissociated' state. This is only speculation, however, and although one-ended dissociation probably provides a path for a large part of the racemisation it is quite possible that some other mechanism involving bond rotation rather than bond breaking[14-16] plays some part. A twist mechanism has been proposed for the inversion of $Co(ox)_3^{3-}$,[1,17] which apparently[1] proceeds without one-ended dissociation of the oxalate group, and the possibility of twist mechanisms playing a large part in the metal ion-catalysed racemisation of $Cr(ox)_3^{3-}$ is discussed by Shooter.[18] The dependence of the rate of racemisation of $Cr(ox)_3^{3-}$ on acid concentration appears to be quite different from the dependence on metal-ion concentration and hence it is possible that in one case a route *via* a one-end dissociated species might predominate while in the other a twist mechanism might be favoured.

[1/1339 *Received, 2nd August*, 1971]

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[12] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

[13] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1899.

[14] P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, 1943, **20**, 81.

[15] J. C. Bailar, jun., *J. Inorg. Nuclear Chem.*, 1958, **8**, 165.

[16] C. S. Springer and R. E. Sievers, *Inorg. Chem.*, 1967, **6**, 852.

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

[18] D. Shooter, Thesis, University of Auckland, 1969.