The Reactivity of Co-ordinated Oxalate. Part VII.[1] Specific Salt Effects in the Racemisation of the Trisoxalatochromium(III) Anion {$[Cr(ox)_3]^{3-}$}

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The effect of changes of cation (M) in the salt $M_3Cr(ox)_3$ on the observed rate of racemisation of the $[Cr(ox)_3]^{3-}$ anion have been investigated in aqueous solution at 25 °C, (where M = Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Me_4N^+, Et_4N^+, $Pr^n{}_4N^+$, and $Bu^n{}_4N^+$). In the presence of the alkali-metal ions and the ammonium ion the observed rates of $[Cr(ox)_3]^{3-}$ racemisation were similar but decreased with increasing size of the R_4N^+ ion. Increasing the concentration of Et_4N^+ (Et_4NI) caused further decreases in the observed racemisation rate. These data are interpreted in terms of specific ion interactions, with $[Cr(ox)_3]^{3-}$ participating in 'water structure enforced ion-pairing' with the R_4N^+ ions. The $Et_4N^+ \cdots [Cr(ox)_3]^{3-}$ ion-pair formation constant and the specific racemisation rate constant of $[Cr(ox)_3]^{3-}$ in the ion-pair have been determined by curve fitting to be 26 and $18{\cdot}7 \times 10^{-3}$ min^{-1} respectively.

Changes in concentration of the added salts $NaClO_4$, NH_4NO_3, and NaI on the observed rate of $[Cr(ox)_3]^{3-}$ racemisation have also been investigated in aqueous solution at 25 °C and the presence of a residual racemisation rate observed. This racemisation is thought to occur by interaction with the solvent. This view is supported by rate studies in mixed solvents and results of these are compared with earlier results.

ALTHOUGH the intramolecular[2] racemisation of $[Cr(ox)_3]^{3-}$ has been studied in aqueous acids,[3] in the presence of metal ions,[4-6] in mixed solvent systems,[7,8] and even in the solid state,[9-11] little attention has been paid to the details of the effect of the cation (M) in the salt $M_3Cr(ox)_3$ on the racemisation in aqueous solution. Billardon[12] has reported that the rates of racemisation of the salts $K_3Cr(ox)_3$ and $K_6(strychnine)_2Cr(ox)_3$ are similar in aqueous solution at 20 °C. Kernohan *et al.*[6] have reported a dependence of the observed rate of racemisation of $[Cr(ox)_3]^{3-}$ on M for the series M = Li^+, Na^+, K^+ and Cs^+. This dependence was related, in part, to changes in cation size. The effect of this series of cations has now been re-examined and extended to include Rb^+, NH_4^+ and some symmetrical tetra-alkylammonium cations. The racemisation rate of $[Cr(ox)_3]^{3-}$ in aqueous solution which occurs with only M present has been measured at various temperatures.[4,5,7,8,13]

An entirely satisfactory model for the role of the cation in the racemisation process is still wanted.

EXPERIMENTAL

Preparation of Compounds.—Potassium trisoxalatochromium(III) trihydrate was prepared by a literature method[14] [Found: Cr, 10·7; $(C_2O_4)^{2-}$, 54·25. Calc. for $K_3Cr(C_2O_4)_3,3H_2O$: Cr, 10·65, $(C_2O_4)^{2-}$, 54·2%.] Tetramethylammonium iodide and tetraethylammonium iodide were prepared by allowing the appropriate alkyl iodide and trialkylamine to react, with subsequent recrystallisations from water. Tetrapropylammonium iodide and tetrabutylammonium iodide (Fluka AG) were used without further purification. Analysis showed these tetra-alkylammonium iodides to be anhydrous. Glycerol (Riedel-De Haen) was dried at 180 °C.[15] 1,4 Dioxan (Riedel-De Haen) was purified by a standard method.[16]

All other reagents were of the purest available grade and used without further purification.

The resolved strychnine salt of the $[Cr(ox)_3]^{3-}$ anion was obtained by the method of Werner[17] as modified by Schweitzer and Lee.[18] Liberation of the anion from the strychnine salt was achieved by the precipitation of strychnine iodide. Two precipitation methods were employed. (1) Where the resolved $[Cr(ox)_3]^{3-}$ salt was insoluble in acetone or ethanol (Li^+, Na^+, K^+ and Rb^+) the dried strychnine salt was mixed with a slight excess of the appropriate iodide, the mixture was cooled in an ice–water bath, and a small quantity of pre-cooled water was added. After precipitation the resulting paste was liquified and quickly filtered and the filtrate was passed into acetone or ethanol. The resolved $[Cr(ox)_3]^{3-}$ salt was then filtered off, washed, and dried. This low-temperature method gives better $[Cr(ox)_3]^{3-}$ resolution than the usual method which is performed at ambient temperatures.

(2) For the other $[Cr(ox)_3]^{3-}$ salts used, a weighed quantity of the appropriate iodide was dissolved in water (0·5 ml) and brought to the run temperature. An excess of the strychnine salt was added and the solution was shaken for about a minute. The precipitate was filtered off and the filtrate was diluted to the required concentration by water or a solution containing the added salt; it was used immediately in a run. No precipitate of strychnine iodide was observed when the filtrate was added to a solution of sodium iodide.

Optical rotation measurements at 494 nm were made using a Schimadzu QR-50 spectrophotometer with a polarimeter attachment.

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

[2] F. A. Long, *J. Amer. Chem. Soc.*, 1939, **61**, 570.

[3] A. L. Odell and D. B. Rands, unpublished results.

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

[5] E. Bushra and C. H. Johnson, *J. Chem. Soc.*, 1939, 1937.

[6] J. A. Kernohan, A. L. Odell, R. W. Olliff, and F. B. Seaton, *Nature*, 1966, **209**, 906.

[7] G. K. Schweitzer and J. L. Rose, *J. Phys. Chem.*, 1952, **56**, 428.

[8] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, 1962, **1**, 531.

[9] C. H. Johnson, *Trans. Faraday Soc.*, 1935, **31**, 1612.

[10] C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, 1935, **31**, 1621.

[11] C. D. Schmulbach, J. Brady, and F. Dachille, *Inorg. Chem.*, 1968, **7**, 287.

[12] M. Billardon, *J. Chim. Phys.*, 1964, **61**, 1070.

[13] E. K. Rideal and W. Thomas, *J. Chem. Soc.*, 1922, **121**, 196.

[14] 'Inorganic Synthesis,' ed. H. S. Booth, McGraw-Hill, New York, 1939, vol. 1, p. 37.

[15] A. I. Vogel, 'A Text-Book of Practical Organic Chemistry,' Longmans, Green and Co., London, 1948.

[16] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon Press, London, 1966.

[17] A. Werner, *Ber.*, 1912, **45**, 3061.

[18] G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, 1952, **56**, 195.

The polarimeter tubes (20-cm) were contained in a thermostated compartment maintained at 25·0 ± 0·05 °C.

For all runs a plot of optical rotation against time was always found to be exponential, indicating a first-order loss of optical activity. For each run a least-squares fit of a Guggenheim [19] plot was used to obtain the observed rate of $[Cr(ox)_3]^{3-}$ racemisation. Usually 26 points were obtained for the plot.

The light source of the spectrophotometer (30 W tungsten lamp) caused no observable photochemical racemisation.

RESULTS

The revised values of the observed rates of racemisation of $[Cr(ox)_3]^{3-}$ (k_{obs}) for the alkali-metal cations and the values for the additional cations studied are given in Table 1.

TABLE 1

k_{obs} Values for $M_3Cr(ox)_3$ at 25 °C in aqueous solution. Conc. of $[Cr(ox)_3]^{3-}$ 2·14 × 10^{-3}M

M	k_{obs} × 10^3/min^{-1} (±1½%)
Li^+	37·4
Na^+	37·7
K^+	37·4
Rb^+	37·6
Cs^+	37·2
NH_4^+	37·9
Me_4N^+	35·9
Et_4N^+	34·0
$Pr^n{}_4N^+$	32·5
$Bu^n{}_4N^+$	32·3

The dependence of k_{obs} on added salt concentration is given in Figure 1. An insert has been included to show the extent of the extrapolation required to obtain the residual racemisation rate (k_0). Also shown in the insert is the dependence of k_{obs} on NaI concentration. Over the NaI concentration range studied, no difference was detected between the observable effects of NaI and $NaClO_4$.

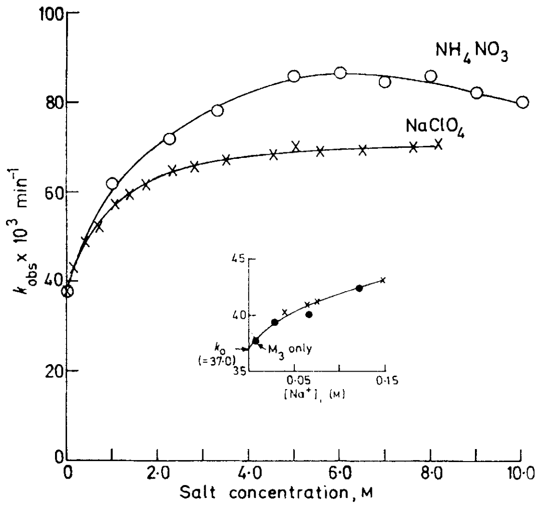

FIGURE 1 Dependence of k_{obs} on added salt concentration at 25 °C (Inset, ● NaI, × $NaClO_4$)

Table 2 gives the dependence of k_{obs} on Et_4N^+ concentration. The concentration changes were made by adding the resolved $(Et_4N)_3Cr(ox)_3$ to an aqueous solution containing varying amounts of Et_4NI. These data are plotted in Figure 2.

TABLE 2

Dependence of k_{obs} on Et_4N^+ concentration at 25 °C in aqueous solution

Conc. of $[Cr(ox)_3]^{3-}$ 2·14 × 10^{-3}M

[Et_4N^+]/M	k_{obs} × 10^3/min^{-1} (±2%)
0·0064	34·0
0·010	33·2
0·019	30·6
0·029	29·1
0·049	27·3
0·079	24·9
0·109	23·0

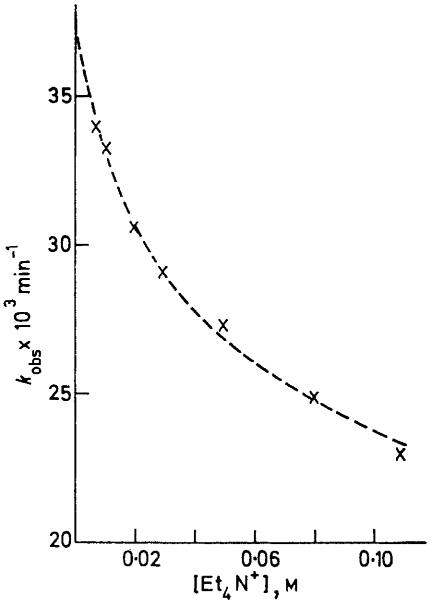

FIGURE 2 Plot of k_{obs} vs. [Et_4N^+] at 25 °C; × = experimental points, — — — calculated with K = 26·0 and k = 18·7 × 10^{-3} min^{-1}

Tables 3 and 4 give the k_{obs} values for the two mixed solvent systems studied.

TABLE 3

Dependence of k_{obs} on glycerol concentration in glycerol–water mixtures at 25 °C

[$Na_3Cr(ox)_3$] = 2·14 × 10^{-3}M

Glycerol (wt %)	k_{obs} × 10^3/min^{-1} (±2%)
0·0	37·7
13·7	33·3
26·4	28·4
37·1	25·2
47·6	21·9
55·9	19·3
61·1	17·4

TABLE 4

Dependence of k_{obs} on dioxan concentration in dioxan–water mixtures at 25 °C

[$Na_3Cr(ox)_3$] = 2·14 × 10^{-3}M

Dioxan (wt %)	k_{obs} × 10^3/min^{-1} (±2%)
0·0	37·7
20·0	12·3
20·0 [a]	12·5
40·0	5·07

[a] Unpurified dioxan.

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[19] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' J. Wiley, New York, 1961, 2nd edn., p. 152.

DISCUSSION

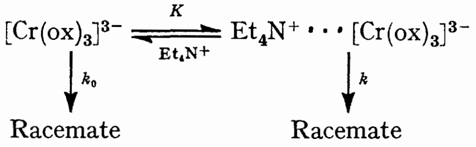
With a $M_3Cr(ox)_3$ concentration of $2{\cdot}14 \times 10^{-3}$M and M = alkali-metal ion or ammonium ion, the rates of $[Cr(ox)_3]^{3-}$ racemisation are equal within experimental error (Table 1). Upon increasing the concentration of M, by the addition of a salt containing M, some rate differences between Na^+ and NH_4^+ are detectable* (Figure 1). Extrapolation to zero M concentration (Insert—Figure 1) gives what we will term the 'uncatalysed' rate of $[Cr(ox)_3]^{3-}$ racemisation (k_0). At 25 °C in aqueous solution $k_0 = 37{\cdot}0 \times 10^{-3}$ min^{-1}. With M = symmetrical tetra-alkylammonium ion, k_{obs} decreases to values below k_0 (Table 1), the magnitude of the decrease depending on the length of the alkyl group. With M = Et_4N^+, addition of further Et_4N^+ (as Et_4NI) causes this decrease in k_{obs} to be accentuated (Figure 2, Table 2).

It is difficult to rationalise the above data in terms of the classical approach to salt effects, as, from conventional ionic strength considerations, the rate-accelerating effect of a 1 : 1 electrolyte (*e.g.* $NaClO_4$) and the rate decelerating effect of another 1 : 1 electrolyte (*e.g.* Et_4NI) are incompatible, unless one introduces rather arbitrary coefficients into some modified form of the Debye–Huckel equation.[19,20] Similar anomalous effects in reaction kinetics have been attributed to R_4N^+ ion-pair formation.[21,22] The existence of ion-pair formation between R_4N^+ ions and $[Cr(ox)_3]^{3-}$ has been established from n.m.r. measurements by Kelm *et al.*[20]

The sensitivity of k_{obs} towards changes in M and concentration of added salt, and the associated uncertainty regarding the inertness of any added salt towards $[Cr(ox)_3]^{3-}$ racemisation, discouraged us from using 'constant ionic strength' conditions in this study. If medium effects predominate in an ionic system, the lack of a constant ionic strength could lead to misleading conclusions. However, in systems where ion-pairing is known or thought to occur to a kinetically significant extent and where the 'inertness' of an added electrolyte is in doubt, the omission of such an electrolyte can be advantageous.

From our data (Table 2) it is now possible to obtain a value for the formation constant (K) for the $Et_4N^+ \cdots [Cr(ox)_3]^{3-}$ ion-pair, and to obtain the specific rate constant of $[Cr(ox)_3]^{3-}$ racemisation in this ion-pair.

If it is assumed that $[Cr(ox)_3]^{3-}$ predominates over I^- in a fast equilibrium ion-pair formation with the Et_4N^+ ions and that, over the concentration range studied, $[Cr(ox)_3]^{3-}$ and Et_4N^+ associate in the ratio 1 : 1, then the following reaction scheme can be proposed:



Without making any assumptions regarding the degree of ion-pairing, it is possible by curve fitting to obtain unique values of K and k. This arises because the curvature of the k_{obs} *vs.* $[Et_4N^+]$ plot is governed by K alone.

The best fit values obtained were: $K = 26 \pm 5$; $k = 18{\cdot}7 \pm 3 \times 10^{-3}$ min^{-1}. The quality of fit can be seen in Figure 2.

This interpretation of our kinetic data does not take into account activity coefficient changes which might occur with changes in ionic strength, but rather uses the concept of the semi-ideal solution introduced by Scatchard.[23] Such a solution is defined by Stokes and Robinson [24] as 'one in which all departures from ideal behaviour are attributed to chemical reactions, and the activity of each actual species in the solution is equal to its actual mole fraction when the chemical reactions have reached equilibrium'. This approach permits a quantitative treatment of the data while eliminating the difficulties associated with the calculation of ion-activities. In $[Cr(ox)_3]^{3-}$ racemisation these difficulties arise because of the magnitude of the charge on $[Cr(ox)_3]^{3-}$, the high concentration of $[Cr(ox)_3]^{3-}$ which was necessary to obtain sufficient optical rotation, and the possibility of specific ion-interactions which would not be taken into account by the Debye–Huckel equation or its modifications. Difficulties also arise in the prediction of ionic strength effects on k, as the nature of the transition state of $[Cr(ox)_3]^{3-}$ racemisation is uncertain and may involve only a small charge separation.

The decreases in k_{obs} caused by increasing the size of the R_4N^+ ion (Table 1) can be understood in terms of known R_4N^+ ion-interactions. Of the types of interaction which have been suggested [25,26] as being responsible for R_4N^+–halide ion-pairs, 'water structure enforced ion-pairing' has been said [27] to predominate with I^- salts. If I^-, because of its size and small degree of hydration (compared with Cl^- or Br^-), can promote this type of ion-pairing, then when $[Cr(ox)_3]^{3-}$ is present it should predominate over I^- in any association of this type with the R_4N^+ ions.

The term 'hydrophobic bonding' has been used to describe water structure enforced ion-pairing and this occurs [26] when two (or more) non-polar groups come into contact, thereby minimising the disturbance to the water structure, and it is said to occur to a greater extent the larger the cation. Thus the observed decreases in k_{obs}

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* From similarity between the dependence of k_{obs} on $NaClO_4$ and NaI concentrations (Insert—Figure 1), one concludes that the anion of an added salt has little effect on k_{obs} over the concentration range investigated, a similar conclusion was reached by Beese and Johnson.[4]

[20] H. Kelm, H. Steiger, and G. M. Harris, *Z. Phys. Chem. (Frankfurt)*, 1969, **67**, 98.

[21] J. L. Kurz and C. D. Gutsche, *J. Amer. Chem. Soc.*, 1960, **82**, 2175.

[22] E. F. J. Duynstee and E. Grunwald, *J. Amer. Chem. Soc.*, 1959, **81**, 4540, 4542.

[23] G. Scatchard, *J. Amer. Chem. Soc.*, 1921, **43**, 2387.

[24] R. H. Stokes and R. A. Robinson, *J. Phys. Chem.*, 1966, **70**, 2126.

[25] S. Lindebaum and G. E. Boyd, *J. Phys. Chem.*, 1964, **68**, 911.

[26] R. Diamond, *J. Phys. Chem.*, 1963, **67**, 2513.

[27] D. W. Larsen and A. C. Wahl, *Inorg. Chem.*, 1965, **4**, 1281.

can be attributed to variations in the extent of the ion-pairing between $[Cr(ox)_3]^{3-}$ and R_4N^+ ions. However changes in the specific rate constant k could also be influential. A study of the concentration dependence of k_{obs} with the various R_4N^+ ions present should help to clarify this situation.

Since the R_4N^+ ions do not possess a co-ordinated primary hydration sphere,[26] their association with $[Cr(ox)_3]^{3-}$ may exclude solvent water from the $[Cr(ox)_3]^{3-}$ solvation sphere. The presence of an ' uncatalysed ' path for $[Cr(ox)_3]^{3-}$ racemisation, which indicates that this path occurs by interaction between complex anion and water alone, and the observed decreases in k_{obs} with increasing Et_4N^+ concentration, suggest that this exclusion of solvent water results in a slower $[Cr(ox)_3]^{3-}$ racemisation. Further indication of the importance of water in $[Cr(ox)_3]^{3-}$ racemisation has been obtained from studies of the racemisation in mixed solvent systems,[7,8] where the rate has been found to decrease with increasing concentration of the non-aqueous component of the solvent. Also, as noted by Johnson,[9] the solid-state racemisation of $K_3Cr(ox)_3$ proceeds ' faster and further ' in the hydrated salt at room temperature than in the anhydrous salt at 115 °C.

Changes in the charge of an added cation have been shown [4] to influence dramatically the rate of $[Cr(ox)_3]^{3-}$ racemisation. The low value of k ($= 18{\cdot}7 \times 10^{-3}$ min^{-1}, *cf.* $k_0 = 37{\cdot}0 \times 10^{-3}$ min^{-1}) could thus be attributed to a reduction in the surrounding charge density occurring as Et_4N^+ replaces solvent water in the vicinity of a complex anion.

Alternatively, the slower racemisation could be the result of the relative orientation of $[Cr(ox)_3]^{3-}$ and Et_4N^+ in the ion-pair either prohibiting or hindering one-ended-dissociation of an oxalate ligand, or prohibiting a twisting motion through a rigidifying of the $[Cr(ox)_3]^{3-}$. One can also propose that one-ended-dissociation is not hindered, but that the dissociated end of the oxalate ligand is forced to return to its original position. Of these alternatives, we favour the exclusion of water from the solvation sphere of $[Cr(ox)_3]^{3-}$ because of the additional observation that large non-hydrophobic cations such as $Zn(en)_3^{2+}$ do not cause a decrease in k_{obs}.[4]

A comparison of K with other formation constants is difficult because of the rather unusual form of ion-pairing proposed. However Larsen and Wahl [27] have obtained a similar value, of 8 at 25 °C, for the equilibrium quotient for association between the triply charged ion $Fe(CN)_6^{3-}$ and Et_4N^+ in aqueous solution.

Glycerol–water and Dioxan–water.—In this study we found the k_{obs} values for the dioxan–water system to be smaller (by a factor of approximately a half) than those determined by Schweitzer and Rose [7] under similar conditions. (The purity of the dioxan did not appear to be critical, Table 4). A similar discrepancy has been found by Spees and Adamson,[8] who measured a half-life of $[Cr(ox)_3]^{3-}$ racemisation in a 30 mol % ethanol solution at 35 °C of 56 min whereas under similar conditions Schweitzer and Rose found a half-life of 18 min. There is, however, general agreement that k_{obs} decreases with increasing concentration of the organic component.

A comparison of the data in Tables 3 and 4 shows that at comparable concentrations, k_{obs} is smaller with dioxan than with glycerol. However no linear relationship could be found between k_{obs} and water activity, dielectric constant, or concentration of organic component, but the indication is that a ' water-like ' solvent is necessary for the ' uncatalysed ' racemisation of $[Cr(ox)_3]^{3-}$.

[1/579 *Received, April 19th, 1971*]