Inorganica Chimica Acta, 12 (1975) L11 - L12

Medium Effects in the Aquation of Potassium Tris(oxalato)chromate(III)

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(Received November 14, 1974)

Following the earlier work on the aquation of trisoxalatochromate(III) anions,[1] studies dealing with the effect of temperature, acidity, and ionic strength have been published.[2-4] An oxalate ring opening–closing mechanism[5] has been generally accepted, although the detailed mechanism is controversial.[1,2]

The published results on the salt effects, obtained at high acid concentration, emphasised the acid-catalysed reaction path. The rate constants were calculated assuming that the aquation reaction leads only to the *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ isomer.[3] This assumption has been recently questioned.[6]

In the present investigation, a low acid concentration was maintained while the ionic strength or the dielectric constant were varied. Only a small change of pH was observed when the reaction seemed virtually complete.

Experimental

Potassium trisoxalatochromate(III), $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ was prepared, recrystallised and analysed as described elsewhere.[7] It assayed Cr, 10.6; $(C_2O_4)^{2-}$, 52.9; H_2O, 10.7% (calc. Cr 10.66; $(C_2O_4)^{2-}$, 54.19; H_2O, 11.09%). The molar decadic extinction coefficients of aqueous solutions at the absorption peaks agreed with the published data.[7,8]

Dioxan was dried by sodium hydroxide, refluxed over sodium and then fractionally distilled. The physical constants of the purified liquid were in good agreement with the published constants. All the other chemicals used were of AnalaR or similar grade.

Solutions of the complex salt and of hydrochloric acid were thermostatted at 90° ± 0.2 °C before thorough mixing. The final solution was 5×10^{-3} *M* in the complex ion and in hydronium ions. Aliquots were withdrawn at intervals, quenched and then diluted before measuring the absorbance, D_t, at the absorption peaks using a Unicam SP500 spectrophotometer. The final reading, D_∞, was determined experimentally by leaving solutions at 95 °C for a long time. The linear variation of $\log(D_t - D_\infty)$ with time indicated first order kinetics.

The dielectric constant of water/dioxan solutions was measured as described elsewhere[9], thermostatting the cell to ± 0.03 °C.

Results and discussion

Fig. 1 shows the linear variation of the logarithm of the rate constant, $\log k$, with the ionic strength, μ.[10] Each constant is the mean of the results at the two visible absorption maxima.

Under the experimental conditions used, the results seem to fit the relation:[11]

$$\ln k = \ln k_0 + (b_A + b_B - b)\mu \qquad (1)$$

where the b terms refer to the reactants A, B and the activated complex respectively. A decrease in the rate constant of the reaction between an ion and a polar molecule has been tentatively ascribed by Benson to a positive interaction between the ion atmosphere with the dipole moment of the molecule.[12]

Equation (1) does not predict any specific effect of the added salt. However, the results in Fig. 1 show that the difference between the results using $NaClO_4$ or $NaNO_3$ was greater than the experimental error.

Odell and Shooter[13] have reported higher rate constants of racemisation of $[Cr(C_2O_4)_3]^{3-}$ in NH_4NO_3 than in $NaClO_4$ solutions, although the rate of racemisation of $Na_3[Cr(C_2O_4)_3]$ was similar to that of $(NH_4)_3[Cr(C_2O_4)_3]$. However, they did not

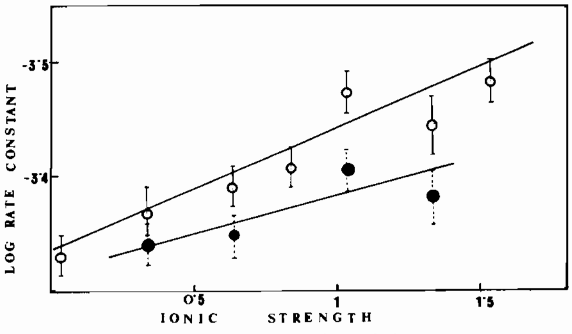

Fig. 1. The variation of the logarithm of the rate constant with ionic strength: ○, $NaClO_4$; ●, $NaNO_3$.

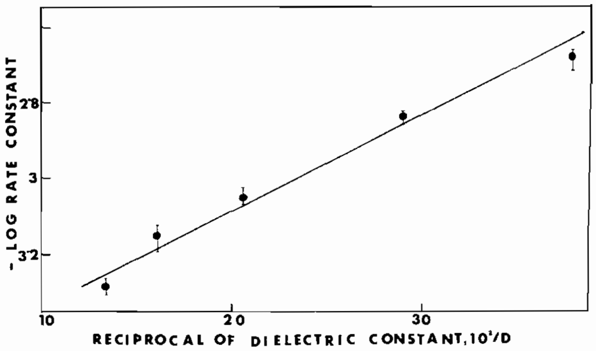

Fig. 2. The variation of the logarithm of the rate constant with the reciprocal of the dielectric constant.

discuss the role of the anion. The small difference between perchlorate and nitrate solutions (Fig. 1) may be tentatively ascribed to the greater hydration of ClO_4^- compared to NO_3^-.[14] This would result in a slower aquation of $[Cr(C_2O_4)_3]^{3-}$ in perchlorate than in nitrate solutions.

The linear variation of log*k* with the reciprocal of the dielectric constant, in water–dioxan solutions, is depicted in Fig. 2. These results are in agreement with the Laidler–Eyring equation,[11] which predicts that the variation of ln*k* with the reciprocal of the dielectric constant would be linear with a positive slope, for a reaction involving an ion and a molecule.

Conclusion

Although hydronium ions catalyse the aquation of $[Cr(C_2O_4)_3]^{3-}$ in acidic solutions, it seems that, under the conditions we used, the rate-determining step involves a $[Cr(C_2O_4)_3]^{3-}$ ion and a water molecule.

References

1 K. V. Krishnamurty and G. M. Harris. *J. Phys. Chem., 64,* 346 (1960).
2 C. A. Bunton, J. H. Carter, D. R. Llewellyn, A. L. Odell and S. Y. Hih, *J. Chem. Soc.,* 4622 (1964).
3 D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem., 27,* 1643 (1965).
4 H. Kelm and G. M. Harris, *Inorg. Chem., 6,* 1743 (1967).
5 D. R. Llewellyn and A. L. Odell, *Proc. Australian Atomic Energy Symposium, 5,* 623 (1958).
6 M. W. Rophael and M. A. Malati, *J. Chem. Soc. A,* 1903 (1971).
7 M. A. Malati and A. A. Abdul Azim, *Egypt. J. Chem., 2,* 47 (1959).
8 H. L. Schlafer, H. Gausmann and W. Tausch, *Z. phys. Chem. Frankf., 43,* 113 (1962).
9 M. W. Rophael and M. A. Malati, *J. Inorg. Nucl. Chem., 36,* 1355 (1974).
10 When log*k* was plotted against μ for the first three points, the plot departed from linearity to a greater extent than Fig. 1. The slope of the best-fitting line was appreciably smaller than -3.
11 K. J. Laidler, "Chemical Kinetics", McGraw Hill, New York, pp. 130 - 131 (1950).
12 S. W. Benson, "The Foundations of Chemical Kinetics", McGraw Hill, New York, pp. 536 - 7 (1960).
13 A. L. Odell and D. Shooter, *J. Chem. Soc. (Dalton Trans.* 135 (1972).
14 E. Glueckauf, *Trans. Faraday Soc., 51,* 1235 (1955).