

The Acid Hydrolysis and Related Reactions of Oxalatobis(2,2'-bipyridine)chromium(III) and Oxalatobis(1,10-phenanthroline)-chromium(III) Ions

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The kinetics of the acid hydrolysis of Cr(ox)-(bipy)₂⁺* and Cr(ox)(phen)₂⁺ have been studied. The rate expression is $\text{rate} = k_{\text{aqn}}[\text{H}^+][\text{complex}]$. At 25 °C and unit ionic strength the respective second order rate constants are: $k_{\text{aqn}} = 9.0 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ and $5.9 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$. The activation parameters have been measured, and the enthalpies of activation are the same as those reported for the racemisation of the same complexes. This is consistent with the major contribution to ΔH^\ddagger being the breaking of a Cr—O bond in a common intermediate.

Although much studied^{1,2} the mechanisms of reactions involving transition metal complexes containing coordinated oxalate still pose problems. In particular, it has recently been shown² that the oxygen-18 exchange and the racemisation of the title complexes follow different rate laws. The activation parameters for the ¹⁸O exchange, unlike the racemisation, differ very little on substitution of Cr³⁺ for Co³⁺³ or for Pt²⁺⁴ or on substitution of L-L for oxalate.² The exchange thus reflects the *ligand reactivity* and has been rationalised^{1,2} in terms of proton attack on the carbonyl oxygen of the complexed oxalate.

Analogous solvent or proton attack on the coordinated oxygen would lead to *disruption of the octahedral structure* (Cr—O bond stretch-

ing) with racemisation through an idealised five coordinate, or, if extra solvated water is available, through a seven coordinate intermediate. The latter but not the former would accord with the now accepted associative mechanism⁵ for substitution in Cr³⁺ complexes, and on further proton or solvent attack would lead to disruption of both metal—oxygen bonds and aquation. The title complexes are known on aquation to give the *cis*-diaqua-(L-L)₂ complexes although more slowly than the rate at which racemisation occurs.

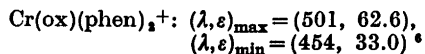
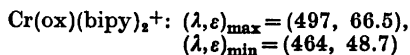
Since the major contribution to the activation energy would, following the above mechanism, in *both cases* be the stretching of the metal—oxygen bond, similarities in the activation energies of the two processes might be expected. The extra step after racemisation and leading to dissociation of oxalate depend on rapid equilibria involving solvent molecules brought into the transition state by proton or metal ion attack on the coordinated oxygen. We present here the kinetic data for the acid hydrolysis and discuss this together with the data for the related reactions given in the literature.

EXPERIMENTAL

[Cr(ox)(bipy)₂] Cl·4H₂O and [Cr(ox)(phen)₂] CF₃COO·2H₂O were prepared from the respective "diols" by treating the diols for about 12 h with equimolar amounts of oxalic acid and potassium oxalate at 50 °C. The products were

* The following abbreviations are used in this paper: phen=1,10-phenanthroline, bipy=2,2'-bipyridine, ox=oxalate ion, and L-L=bipy or phen.

recrystallised from water and the purity was confirmed by means of the visible spectra of the aqueous solutions:



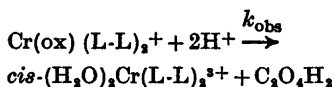
Due to the low solubilities of the perchlorate complex salts, nitric acid (Merck *pro analysi*) was used throughout. Preliminary experiments showed that this acid gave the same results as did hydrochloric acid. The ionic strength was kept constant at 1.0 M with either sodium nitrate or lithium nitrate, neither of these cations giving specific rate effects. Water redistilled twice in an all quartz apparatus was used for making up all the stock and experimental solutions.

The spectra of the complexes were measured in the range 600–350 nm using a Zeiss DMR 10 double grating spectrophotometer. An accurately weighed amount of the solid complex was quickly dissolved in a thermostatted solution of the other reagents, making the concentration of the complex $1-7 \times 10^{-3}$ M. The solutions were then immediately transferred to the thermostatted spectrophotometer cell and the reaction was followed by measuring the absorbancies at λ_{max} (497 nm for Cr(ox)(bipy)_2^+ and 501 nm for Cr(ox)(phen)_2^+).

The kinetic data were collected on punched paper tape by means of an automatic data sampling system and fed into a UNIVAC 1110 computer for analysis. The reactions were, with the exception of the lowest temperature, followed for at least two half lives and there were always at least 2000 measurements per kinetic run.

RESULTS

The spectra of the final solutions were those of the *cis*-diaqua complexes, and the overall reaction is therefore



Pseudo first order rate constants, k_{obs} were determined by minimising the error square sum, $s^2 = \sum_{i=1}^n (A_{\text{obs}} - A_{\text{calc}})^2$ where n is the number of measurements, A_{obs} is the measured absorbancy at the fixed wavelength, and A_{calc} the absorbancies calculated from

$$A_{\text{calc}} = (A_0 - A_\infty) \exp(-k_{\text{obs}}t) + A_\infty$$

where A_0 and A_∞ are the absorbancies at $t=0$ and $t=\infty$, respectively. The minimum of s^2 with respect to k_{obs} was found by means of a random search procedure written in NU-algol.

The above procedure was possible as the experiments were always performed under conditions in which the acid concentrations were held virtually constant during the reaction. The results from the computer analysis showed that the reactions were first order in complex. This was further confirmed by determining the rate constants with different initial concentrations of the complexes under otherwise identical conditions.

Examples of the effect of acid concentration on the rate of aquation are shown in Fig. 1. The results show that the reaction is first order in H^+ both for the phen and the bipy complex—in contrast to the racemisation reaction (see discussion below). Since the straight lines in all cases within experimental error go through the origin there is no detectable acid independent dissociation reaction.

Addition of oxalic acid to the reaction mixtures had no influence on the reaction rates, *i.e.* the reverse reaction is negligible.

Table 1 gives the second order rate constants, k_{aqn} determined from the slopes of the straight lines at the different temperatures, together with the enthalpies and entropies of activation calculated from the Eyring plots shown in Fig. 2. Errors are the standard deviations of the least squares plots. The activation parameters for the racemisation reactions of the same complexes under analogous con-

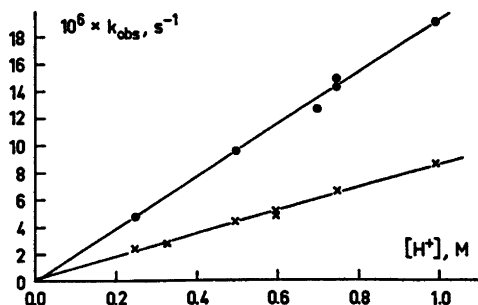


Fig. 1. Acid concentration dependence of aquation rate constants for Cr(ox)(bipy)_2^+ at 46.0 °C and unit ionic strength (x) and for Cr(ox)(phen)_2^+ at 55.8 °C (●).

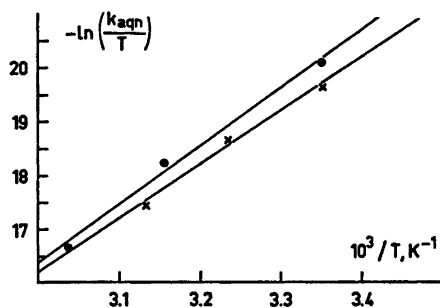


Fig. 2. Eyring plots for aquation of Cr(ox)(bipy)₂⁺ (x) and Cr(ox)(phen)₂⁺ (●).

ditions calculated from Ref. 2 are given in parentheses.

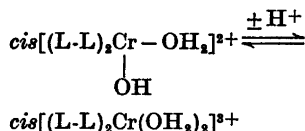
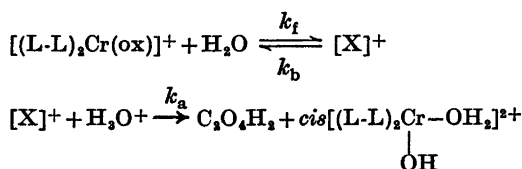
Table 1. Second order rate constants and activation parameters for the acid hydrolysis of the chromium(III) complexes.

$k_{\text{aqn}} \times 10^6$ $\text{M}^{-1} \text{s}^{-1}$	T K	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹
Cr(ox)(bipy) ₂ ⁺			
0.90(6)	298.2	82.4(30)	-84(6)
2.5(1)	309.0	[79.5(10)] ^a	[-61(3)] ^a
8.5(4)	319.2		
Cr(ox)(phen) ₂ ⁺			
0.59(3)	298.2	88.9(50)	-67(8)
3.9(2)	316.7	[82.9(10)] ^a	[-57(3)] ^a
19.2(6)	329.0		

^a Activation parameters for the racemisation of the same chromium (III) complexes calculated from Ref. 2.

DISCUSSION

The mechanism given below can explain that, although the rate laws are different for the racemisation and aquation reactions, the activation enthalpies are within the experimental error the same. It is analogous to that suggested for the reactions of Cr(ox)₃³⁻⁵



In this scheme the major contribution to ΔH^\ddagger arises from the breaking of a Cr-O bond following attack of water on the metal centre. The intermediate [X]⁺ could either reform into the opposite optical isomer or react further by addition of H₃O⁺ to a carbonyl oxygen followed by rapid proton transfer. Following this scheme and using both a steady state treatment for [X]⁺ and the assumption that $k_a[H^+] \ll k_b$ gives

$$k_{\text{rac}} = k_f \text{ and } k_{\text{aqn}} = k_f k_a / k_b$$

For [Cr(phen)₂(ox)]⁺ at 55 °C from Ref. 2, k_{rac} is available. Combining this with our value for k_{aqn} gives $k_b/k_a = 26$. The assumption made above is therefore valid as, under our experimental conditions, $k_a[H^+]$ would never be greater than about 4 % of k_b .

The racemisation of [Cr(bipy)₂(ox)]⁺ occurs through two reaction paths. From the data given in Ref. 2 we calculate that at 45 °C

$$k_{\text{obs}} = k_{\text{rac}} + \frac{k'K[H^+]}{1 + K[H^+]}$$

$k_{\text{rac}} = 1.6 \times 10^{-4} \text{ s}^{-1}$, $k' = 4.0 \times 10^{-4} \text{ s}^{-1}$, $K = 1.4 \text{ M}^{-1}$, where k_{obs} is the total constant, k_{rac} is that for the hydrogen ion independent path analogous to that above, and k' that for the hydrogen ion dependent path. It seems reasonable that this latter reflects a transition state with a bipy ligand protonated in the *trans* form allowing racemisation but with the Cr-N bond rapidly reforming (*cf.* Ref. 3). Combining the acid independent rate at 55 °C with k_{aqn} at the same temperature gives for this complex $k_b/k_a = 29$. This is nearly the same as that calculated above for [Cr(phen)₂(ox)]⁺.

Finally we have found that just as for the racemisation of the monooxalato complexes² and in contrast to the bisoxalato complexes,¹ no specific cation effects are observed for the aquation reaction using the following cations in concentrations *ca.* $5 \times 10^{-2} \text{ M}$: Ce³⁺, Nd³⁺, Yb³⁺, In³⁺, Zn²⁺, Mn²⁺, Cd²⁺, Hg²⁺.

With Tl³⁺, however, oxidation of the oxalate accompanies a more rapid aquation as would be expected from attack on a carbonyl oxygen

of the coordinated ligand, so that the mechanism would thus involve a step analogous to that suggested in Ref. 2 to explain the $[H^+]$ dependence of the ^{18}O exchange. Details of this redox reaction will be given in a later publication.

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