

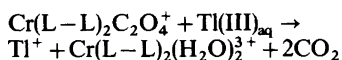
The Oxidation of Captive Oxalate by Thallium(III) in Aqueous Solution*

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The rate of the reaction**



is greater than that for the acid catalyzed aquation of the above chromium complexes. In 1 M nitric acid at 25 °C the respective second-order rate constants for L–L = bipy and phen are: $3.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $2.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. The activation parameters for the same reactions are: $\Delta H^\ddagger = 70 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -75 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H^\ddagger = 69 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -83 \text{ J K}^{-1} \text{ mol}^{-1}$. The reaction is inhibited by chloride. $\text{Cr(bipy)}_2\text{C}_2\text{O}_4^+$ also reacts with Fe(III) and Ce(IV) to give the same diaqua product. The rate-determining step involves electron transfer to the oxidizing cation from the oxalate which is bound to both this and to Cr(III) in a bridged intermediate. No aquation was detected when the above metal ions were replaced by Zn^{2+} , Cd^{2+} , Hg^{2+} , a series of rare earth cations, and also the tris(2,2'-bipyridine)iron(III) ion.

In recent years the reduction of aqueous Tl(III) has been much studied. However apart from the Tl(I)–Tl(III) exchange which occurs by two electron transfer,¹ the presence of Tl(II) as an intermediate

* Some of these results were briefly reported at the XIV International Conference on Coordination Chemistry, Toronto 1972.

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

either has been demonstrated^{2,3} or cannot be eliminated. The present work is a continuation of a series in which the oxidation of the two-electron reducing agent $\text{C}_2\text{O}_4^{2-}$ by Tl(III) has been studied. Thus we have previously found⁴ that oxalic acid and Tl(III) form a complex, TlC_2O_4^+ and have suggested that the redox reaction accompanies the slow decomposition of this complex. In accordance with this oxalate, like chloride, inhibits the two-electron exchange reaction of Tl(I) with Tl(III).⁵ The substitution of bound oxalate by water in the title complexes is acid catalyzed and the mechanism of this has been discussed.⁶ In the present paper we have studied the effect of Tl(III) on the aquation rate of these complexes and attempted to elucidate the mechanism firstly, by comparing the rate of the Tl(III) reaction with other metal ions which also are known to form stable oxalato complexes or to be efficient oxidants and secondly, by comparing the activation parameters for the oxidation by Tl(III) of oxalate bound to Cr(III) and for free oxalic acid.

EXPERIMENTAL

Details of the preparation of $[\text{Cr(bipy)}_2\text{C}_2\text{O}_4]\cdot\text{Cl}\cdot 4\text{H}_2\text{O}$ and $[\text{Cr(phen)}_2\text{C}_2\text{O}_4]\text{CF}_3\text{COO}\cdot 2\text{H}_2\text{O}$ together with the spectral properties of these compounds are given elsewhere.⁷

Due to the low solubilities of the perchlorate complex salts, nitric acid (Merck *pro analysi*) was used throughout. A Tl(III) nitrate stock solution

was prepared by anodic oxidation of standardized Tl(I) nitrate in 2 M nitric acid. The latter was prepared by dissolving recrystallized thallos carbonate (B.D.H. Laboratory Reagent) in nitric acid. The concentration of Tl(III) was determined gravimetrically with 8-hydroxyquinoline as described elsewhere.⁸

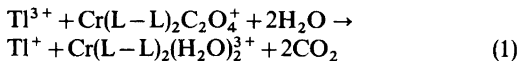
The complex concentrations were about 5 mM or less, while for all reactions the concentration of Tl(III) was in pseudo first-order excess (at least 15-fold). The ionic strength was adjusted to 1.0 M with sodium or lithium nitrate (Merck *pro analysi*). All other chemicals were of reagent grade purity. Water redistilled twice in an all quartz apparatus was used to make up the solutions.

The reaction solutions were kept in a thermostat ($\pm 0.1^\circ\text{C}$). Spectra were measured in the range 700 to 200 nm using thermostatted cells and a Zeiss DMR 10 spectrophotometer. The disappearance of the oxalato complex was followed at an absorption maximum of $\text{Cr}(\text{L}-\text{L})_2\text{C}_2\text{O}_4^+$ (497 nm for L-L=bipy and 501 nm for L-L=phen), the difference between the spectrum of the oxalato and the diaqua complex rendering it possible to follow the reaction spectrophotometrically. Observed absorbance *vs.* time data from individual runs were collected on punched paper tape and analyzed in a UNIVAC 1110 computer.

The formation of Tl^+ was determined by the following procedure: Aliquots of the reaction solution were added to 10 ml of an 8 M aqueous ammonia solution containing 0.5 M sodium chromate, 1 M sodium cyanide, and 10% ethanol. This mixture was cooled in ice and centrifuged. The thallos chromate was washed with ice-cold 10% ethanol, was then redissolved in 10 ml 5 M sulfuric acid, and the amount of Tl^+ was determined from the absorbancy at 208 nm.

RESULTS

a. The effect of Tl(III). The final product has the visible absorption spectrum of the *cis*-diaqua- $(\text{L}-\text{L})_2\text{Cr}(\text{III})$ complex,⁹ and a stoichiometric amount of Tl^+ is formed concomitantly so the overall reaction is (1).



Addition of Tl^+ has no influence on the reaction rate. With excess Tl(III) the absorbance data were treated by standard nonlinear least-squares techniques, minimizing the error square sum

$$s^2 = \sum_n (A_{\text{obs}} - A_{\text{calc}})^2$$

where n is the number of measurements (always greater than 2000), A_{obs} is the measured, and A_{calc} the absorbancy calculated from

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

where k_{obs} is the observed pseudo first-order rate constant, A_0 and A_∞ the absorbancies at $t=0$ and $t=\infty$, respectively. The minimum of s^2 was found allowing k_{obs} , A_0 , and A_∞ to be adjustable parameters.

Excellent first-order kinetics were obeyed over at least 3–4 half lives. The reaction was also first order in Tl(III) in the range covered (1×10^{-2} M to 8×10^{-2} M). k_{obs} was found to be independent of $[\text{H}^+]$ (0.25 to 1.0 M) within the experimental error (*cf.* Table 4). The acid hydrolysis of the oxalato complexes reported earlier⁶ is much slower contributing less than 1% to the above reaction under the present experimental conditions.

The effect of low concentrations of chloride ions on the rate of reaction is illustrated in Fig. 1 and is therefore consistent with (2)

$$k_{\text{obs}} = k_{\text{Tl}^{3+}}[\text{Tl}^{3+}] + k_{\text{TlCl}_2^+}[\text{TlCl}_2^+] \quad (2)$$

No reaction could be detected with sufficient $[\text{Cl}^-]$ to ensure that Tl(III) was predominantly present as TlCl_2^+ which is consistent with complete inhibition by this species. This kinetic effect of chloride

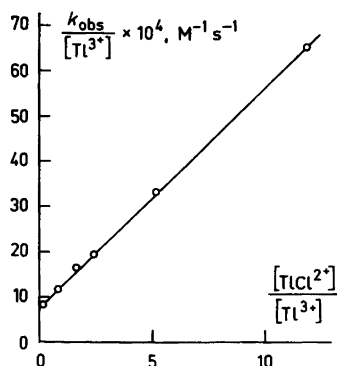


Fig. 1. Chloride ion dependence of k_{obs} for Tl(III) oxidation of $\text{Cr}(\text{bipy})_2\text{C}_2\text{O}_4^+$ at $t=34.7^\circ\text{C}$ and unit ionic strength.

Table 1. Second-order rate constants and activation parameters for the oxidation of the chromium complexes by Tl(III).

T K	$k \times 10^4$ $M^{-1} s^{-1}$	ΔH^\ddagger $kJ mol^{-1}$	ΔS^\ddagger $J K^{-1} mol^{-1}$
Cr(bipy) ₂ C ₂ O ₄ ⁺			
298.2	3.69	70 ± 2	-75 ± 6
299.0	3.64		
307.9	7.54		
313.3	14.0		
318.8	23.9		
327.2	46.5		
Cr(phen) ₂ C ₂ O ₄ ⁺			
298.2	2.36	69 ± 2	-83 ± 6
307.7	6.56		
317.1	12.9		
326.8	30.7		

Table 2. Second-order rate constants and activation parameters for the oxidation of Cr(bipy)₂C₂O₄⁺ by TlCl²⁺.

T K	$k \times 10^4$ $M^{-1} s^{-1}$	ΔH^\ddagger $kJ mol^{-1}$	ΔS^\ddagger $J K^{-1} mol^{-1}$
298.2	1.86	74 ± 2	-67 ± 6
307.9	4.85		
318.8	13.1		
326.7	28.2		

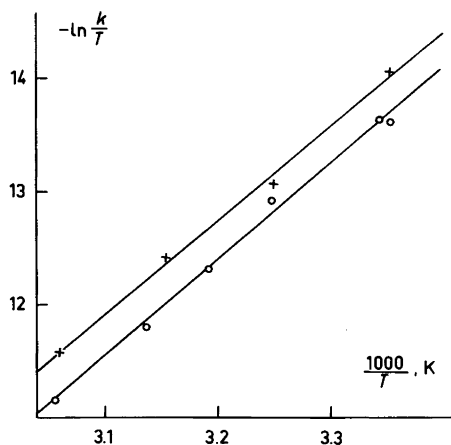


Fig. 2. Eyring plots for oxidation by Tl³⁺ of the Cr(bipy)₂C₂O₄⁺ (O) and Cr(phen)₂C₂O₄⁺ (×) complexes.

Acta Chem. Scand. A 32 (1978) No. 10

Table 3. Stability constants of MC₂O₄⁽ⁿ⁻²⁾⁺, redox potentials of the Mⁿ⁺/M⁽ⁿ⁻¹⁾⁺ couple, and second-order rate constants (k) for the metal ion catalyzed aquation of Cr(bipy)₂C₂O₄⁺. I = 1.0 M and t = 25 °C. Where nothing else is indicated the stability constants are found in Martell, A. E. and Smith, R. M. *Critical Stability Constants*, Vol. 3, Plenum, New York and London, 1977.

Metal ion	K (MC ₂ O ₄ ⁽ⁿ⁻²⁾⁺) M ⁻¹	E° V	k M ⁻¹ s ⁻¹
Ce(IV)	> 10 ⁹ ^a	1.61 ^c	1.1
Tl ³⁺	6.2 × 10 ⁸ ^b	0.30 ^d	3.7 × 10 ⁻⁴
TlCl ²⁺	—	0.19 ^e	1.9 × 10 ⁻⁴
Fe ³⁺	4 × 10 ⁷	0.77 ^c	9.3 × 10 ⁻⁵
Fe(bipy) ₃ ³⁺	—	1.06 ^c	—
In ³⁺	2 × 10 ⁵	—	—
Ce ³⁺	3 × 10 ³	—	—
Nd ³⁺	1.6 × 10 ⁴	—	—
Yb ³⁺	2 × 10 ⁴	-0.58	—
Zn ²⁺	3 × 10 ³	—	—
Cd ²⁺	6 × 10 ²	—	—
Hg ²⁺	~ 10 ² ^a	—	—
Mn ²⁺	66	—	—

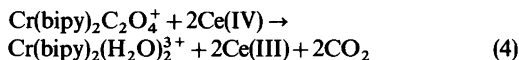
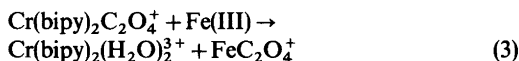
^a Estimated. K for Ce(IV) from known K values for actinides in oxidation state (IV). ^b Ref. 4, corrected to I = 1.0 M. ^c Latimer, W. M. *Oxidation Potentials*, 2nd Ed., Prentice Hall, 1952. ^d Ref. 3 and references therein. ^e Calculated from data in Schwarz, H. A. and Dodson, R. W. *J. Phys. Chem.* 80 (1976) 2543.

is analogous to that known for redox reactions involving Tl(III) as oxidant.

Second-order rate constants, $k = k_{\text{obs}}/[\text{Tl(III)}]$ are given in Table 1 and 2 together with enthalpies and entropies of activation calculated from Eyring plots shown in Fig. 2.

There was no spectral evidence between 700 and 200 nm for any other complex product than the diaqua species shown in (1) (see Discussion).

b. The effect of other metal ions. Of the other metal ions, all in 1.0 M nitric acid, which are given in Table 3, only Fe(III) and Ce(IV) increased the rate of aquation of Cr(bipy)₂C₂O₄⁺. (The effect of the same metal ions on the phen complex has not been studied.) These latter reacted according to (3) and (4)



For the Ce(IV) reaction additional absorption showed the presence of an intensely red intermediate the formation and decay of which could be followed spectrophotometrically. This has previously been detected during the oxidation of free oxalate by Ce(IV) sulfate, was considered to be a 1:1 complex of Ce(IV) and oxalate, and was shown to decompose to give Ce(III) and the oxalate radical, $C_2O_4^{\cdot -}$.¹⁰

DISCUSSION

We calculate that the Tl(III) species present in the reactant solutions are those given in Table 4 which also shows that since the oxidation rate by Tl(III) is within the experimental error independent of $[H^+]$ the major reactant is Tl^{3+} , possibly with a coordinated nitrate.*

The activation parameters for the oxidation of the captive oxalate by Tl(III) are very different from those reported for the oxidation of oxalic acid by Tl(III) ($\Delta H^\ddagger = 102 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = +59 \text{ J K}^{-1} \text{ mol}^{-1}$).⁴ Since the enthalpies of activation found in the present work are about 30 kJ mol^{-1} less than that for the latter reaction then $TlC_2O_4^+$ cannot be an intermediate here.

The ratio between the rates for the bipy and phenoxalato complexes is the same for acid hydrolysis and for Tl(III) oxidation (1.5 at 25°C). In both cases the higher rate of reaction of the bipy complex is due to the entropy term. We therefore suggest a mechanism through an intermediate which is

* Since we found no $[H^+]$ dependence on the rate we have not considered the possible contribution from mixed hydroxo/nitrato complexes.

Table 4. Distribution of Tl(III) among different species in a 1.0 M nitrate solution at different acidities and $t = 25^\circ\text{C}$. K for $TlNO_3^{2+} = 5.0 \text{ M}^{-1}$ at $I = 1.0$ (interpolated) K_d for $TlOH^{2+} = 0.095 \text{ M}$ at $I = 1.0$ (interpolated) $\alpha_{aq} = [Tl^{3+}]/[Tl(III)]$, $\alpha_{OH} = [TlOH^{2+}]/[Tl(III)]$, and $\alpha_{NO_3} = [TlNO_3^{2+}]/[Tl(III)]$. k is the experimentally found second-order rate constant of the $Cr(bipy)_2C_2O_4^+$ reaction.

$[H^+]$ M	α_{aq}	α_{OH}	α_{NO_3}	$k \times 10^4$ $\text{M}^{-1} \text{s}^{-1}$
0.25	.157	.060	.784	3.60
0.50	.162	.031	.808	3.65
0.75	.163	.021	.816	3.65
1.00	.164	.016	.820	3.69

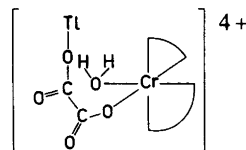
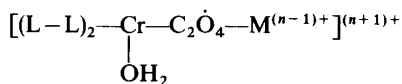


Fig. 3. Suggested intermediate in the oxidation of the oxalato complexes by Tl(III).

formally very similar to the one which we proposed for the acid hydrolysis,⁶ namely the attack of a water molecule on the Cr(III) centre accompanied by breaking of a Cr–O bond and making of a Tl–O bond giving the intermediate depicted in Fig. 3. We do not know whether an NO_3^- is attached to Tl^{3+} and have therefore neither included this in the figure nor in the following discussion. A bridged transition state could also explain the large negative entropy of activation. This intermediate is, however, not sufficient to explain all the facts because a consideration of the data included in Table 3 for all the metal ions clearly shows that for a metal ion to be an efficient aquating agent towards $(L-L)_2CrC_2O_4^+$ it must satisfy two requirements, *i.e.* not only must it be capable of forming a thermodynamically stable oxalato complex but also it must be oxidizing towards the bridging oxalate. The lack of reactivity of $Fe(bipy)_3^{3+}$, which has a high redox potential, shows that fulfilling only one of the requirements is not sufficient and confirms that the accompanying redox reaction must be of the “inner sphere” type. The lower reactivity of $TlCl^{2+}$ when compared with Tl^{3+} can be attributed both to the decreased affinity for oxalate and also to the fact that the redox potential of the $TlCl^{2+}/TlCl^+$ couple is 110 mV less than that of the Tl^{3+}/Tl^{2+} couple.

For the three oxidizing cations studied here the reaction mechanism may be unified if the rate-determining step involves the formation of a precursor complex in which electron transfer can occur and which leads to a reactive intermediate



where $M^{(n-1)+}$ is either Ce(III), Tl(II), or Fe(II) and where a $C_2O_4^{\cdot -}$ radical bridges Cr(III) and $M^{(n-1)+}$. This intermediate differs from that proposed by H. Taube^{11,12} for the oxidation by

Ce(IV) and also by some 2 e oxidants of captive oxalate in $(\text{NH}_3)_5\text{Co(III)C}_2\text{O}_4\text{H}^{2+}$, only in that the C_2O_4^- radical is attached both to the metal centre and to the external oxidizing cation, *i.e.* in that the C_2O_4^- radical is bridging.

On breaking of the second Cr–O bond the oxalate radical is required to be a reducing agent towards Tl(II) ($E^\circ(\text{Tl}^{2+}/\text{Tl}^+)=2.2$ V) and an oxidizing agent towards Fe(II) ($E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})=0.77$ V) giving the thermodynamically stable products, Tl(I) and Fe(III),* respectively. These latter reactions may be so fast that the reactants do not diffuse out of the solvent cage. The Cr(III) centre, however, (unlike the Co(III) centre of $(\text{NH}_3)_5\text{-CoC}_2\text{O}_4\text{H}^{2+}$ of Ref. 11) is unable to accept an electron so that an extra oxidizing cation is required in order to complete the overall Ce(IV) reaction. In agreement with this it is only with Ce(IV) that we have been able to detect an $[\text{M}^{(n-1)+}\text{C}_2\text{O}_4^-]$ complex as a first product.

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* The Fe(III) reaction is thus an example of redox catalyzed substitution.