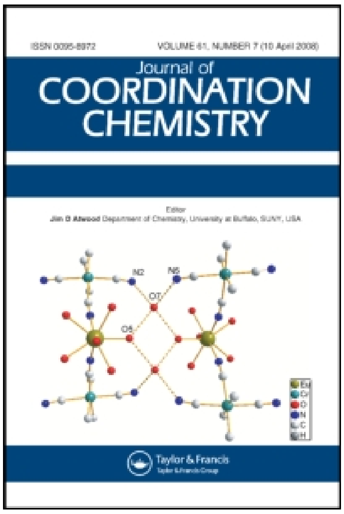

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# MECHANISM OF METAL ION PROMOTED DISSOCIATION OF SOME OXALATO COMPLEXES OF CHROMIUM(III)

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**To cite this Article** Das, Sarmistha , Banerjee, R. N. and Banerjea, D.(1984) 'MECHANISM OF METAL ION PROMOTED DISSOCIATION OF SOME OXALATO COMPLEXES OF CHROMIUM(III)', Journal of Coordination Chemistry, 13: 2, 123 — 129

**To link to this Article: DOI:** 10.1080/00958978408079764

**URL:** http://dx.doi.org/10.1080/00958978408079764

J. Coord. Chem., 1984, Vol. 13, pp. 123–129
0095-8972/84/1302-0123 $18.50/0

# MECHANISM OF METAL ION PROMOTED DISSOCIATION OF SOME OXALATO COMPLEXES OF CHROMIUM(III)

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*(Received September 6, 1982; in final form April 28, 1983)*

Dissociation of oxalato complexes of chromium (III) of the type $[Cr(ox)_n\ (OH_2)_{6-2n}]^{(3-2n)+}$ into $[Cr(ox)_{n-1}\ (OH_2)_{8-2n}]^{(5-2n)+}$ (where n = 1, 3) promoted by different metal ions of the first transition series in acid perchlorate media has been investigated spectrophotometrically. In comparable cases the order of the catalytic activity as measured by the second-order rate constant $k_M$, follows the sequence $Fe^{3+} >> Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$. Log $k_M$ for a particular substrate complex and different promoter metal ions of same charge varies linearly with log $K_{M-ox}$, $K_{M-ox}$ being the formation constant of the *mono*-oxalato complex of the catalysing metal ion $M^{n+}$. The value of $k_{H^+}$ for the acid catalysed reaction occupies a position intermediate between $k_{Co^{2+}}$ and $k_{Mn^{2+}}$, and even for the positively charged complex $[Cr(ox)\ (OH_2)_4]^+$, $Fe^{3+}$ is a far better catalyst than $H^+$, indicating the importance of specific bonding between the promoter and the substrate complex in the intermediate step. These conclusions are corroborated by various free energy relationships and also by comparing results of the present work with literature data on other similar systems. Reactions of a particular substrate complex as promoted by different metal ions and also that by $H^+$ are all practically isoenthalpic.

## INTRODUCTION

For metal ion catalysed reactions, the charge borne by the substrate as well as by the catalysing metal ion may have a significant effect on the kinetic and mechanistic features of the reactions. Thus, for the hydrolysis of an ester, the rate may be either entropy, or enthalpy controlled depending on whether the catalysing metal ion is bipositive or tripositive.[1]

Investigations on the bipositive metal ion catalysed dissociation of some tripositive substrate complexes and the uninegative complex, *cis*-$[Cr(ox)_2(OH_2)_2]^-$ have already been reported from this laboratory.[2,3] The catalysing effect of $Fe^{3+}$ on the dissociation of the latter complex has also been investigated by Choi and Carlyle.[4] It was therefore thought that studies on the effects of bipositive and tripositive metal ions on the dissociation of $[Cr(ox)_3]^{3-}$ and $[Cr(ox)\ (OH_2)_4]^+$ (involving a range of charge interactions) might be worthy of investigation. The only other similar ion on which such studies have been reported to date[5] is $[Co(ox)_3]^{3-}$.

## EXPERIMENTAL

### *Materials and reagents*

Potassium trisoxalatochromate (III) trihydrate was prepared by a known method[6] and

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its purity was checked by chemical analysis and spectral observation ($\lambda_1$, 420 nm, $\epsilon_1$, 96 $M^{-1}$ $cm^{-1}$; $\lambda_2$, 570 nm, $\epsilon_2$, 76 $M^{-1}$ $cm^{-1}$).

Tetraaquomonooxalatochromium (III) perchlorate was prepared in solution following the method of Gourley and Milburn.[7] Chromium contents of this solution were determined spectrophotometrically at 372 nm after oxidising an aliquot to chromate (VI) by alkaline hydrogen peroxide. Oxalate was determined by the method of Hamm.[8] Cr: Oxalate ratios were found to be 1:1.02. Absorbance maxima and corresponding molar absorbances agreed with the reported values.[9]

The metal perchlorates of the catalysing $M^{2+}$ ions were prepared from the corresponding carbonates and perchloric acid. Ferric perchlorate solutions were prepared by digesting freshly precipitated ferric hydroxide with the calculated amount of 1:1 perchloric acid. Metal ion and free acid contents of these solutions were determined using standard procedures.

All other chemicals used were of reagent grade or else purified suitably before use.

### *Apparatus and procedure*

The rates of $Cu^{2+}$, $Zn^{2+}$, $Co^{2+}$ and $Mn^{2+}$ catalysed dissociation of $[Cr(ox)_3]^{3-}$ to *cis*-$[Cr(ox)_2(OH_2)_2]^-$ in acid ($HClO_4$) solution were followed spectrophotometrically at 420 nm which is an absorption maximum for the complex. Since $Ni^{2+}$ also absorbs at this wavelength, the $Ni^{2+}$ catalysed reactions were followed at 560 nm which is another absorption maximum of the substrate complex. At both these wavelengths the difference in the molar absorbance of the substrate and the product complexes is substantial.[10] The reactions were carried out in low acid concentrations where the *tris* complex is known[10] to dissociate to only the *bis* species.

The rate of the $Fe^{3+}$ catalysed dissociation of $[Cr(ox)_3]^{3-}$ was measured by following the formation of $[Fe(ox)]^+$ at 310 nm,[4] while the reaction of $[Cr(ox)(OH_2)_4]^+$ with $Fe^{3+}$ was monitored by following the dissociation of the complex to the product $[Cr(OH_2)_6]^{3+}$ at 560 nm. The $[H^+]/[Fe^{3+}]$ ratio was always kept $\geqslant$ 10, so that practically all the Fe(III) was present in the form of unhydrolysed $Fe^{3+}_{(aq)}$.[11]

Absorbance measurements were made with a Carl-Zeiss (VSU-2P) spectrophotometer against a reference solution which was identical to the experimental solution in every respect except that it did not contain the substrate complex.

Experiments were conducted with the concentration of the catalysing metal ion and the acid in excess compared to that of the substrate complex. The pseudo-first-order rate constants ($k_{obs}$) were evaluated by Guggenheim's method[12] in the case of the $Fe^{3+}$ catalysed dissociation of $[Cr(ox)_3]^{3-}$ and by the usual log $(A_0 - A_\infty)/(A_t - A_\infty)$ *vs* time plot in the case of all the other reactions studied. Reactions were sutided either *in situ* or by a sample quenching technique as needed depending on the rate. Rate plots obtained were linear for up to at least 60% reaction.

## RESULTS AND DISCUSSION

The variation of $k_{obs}$ with catalysing metal ion concentration was in all the cases in agreement with Equation (*1*)

$$k_{obs} = k + k_M [M^{n+}] \qquad (1)$$

where $k_M$ is the contribution due to the $M^{n+}$ catalysed path and k due to the gross acid catalysed ($k_{H^+}$) and spontaneous ($k_s$) paths ($k = k_{H^+} [H^+] + k_s$) if any.[9,10,13] Compared to $k_{Fe^{3+}}$ and $k_{Cu^{2+}}$, k is negligible under the experimental conditions. From the $k_M$ values evaluated from the slopes of $k_{obs}$ *vs* $[M^{n+}]$ plots at different temperatures but under otherwise similar conditions, the values of the activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, where evaluated using the Eyring equation and the least-squares methods. Values of these kinetic parameters along with some relevant literature data[4] on the $Fe^{3+}$ catalysed dissociation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ are given in Tables I and II.

In comparable cases, $k_M$ values for a given substrate complex are in the following sequence of the catalysing metal ions: $Fe^{3+} \gg Cu^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Mn^{2+}$; $H^+$ occupies a position between $Zn^{2+}$ and $Co^{2+}$. Log $k_M$ values for the bivalent metals and for a given substrate complex plotted against log $K_{M-ox}$ ($K_{M-ox}$ being the formation constants of the *mono*-oxalato complexes of the catalysing metal ions) gives a good straight line (see Figure 1) according to the relationship (*2*).

$$\log k_M = A + B \log K_{M\text{-}ox} \qquad (2)$$

This result is similar to what has been observed earlier[3] for the metal ion catalysed dissociation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ (see Figure 1C) and which can also be shown to be valid using literature data[5,14,15] for the metal ion catalysed reactions of several other Cr(III) and Co(IIIO complexes (see Figures 1B[5], 1D[14] and 1E[15] for examples).

The ratios of $k_{Fe^{3+}}/k_{H^+}$ at 25° for the three substrate complexes $[Cr(ox)_3]^{3-}$, *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and $[Cr(ox)(OH_2)_4]^+$ are 3500, 429 and 137 respectively. Thus, even for the positively charged complex $Fe^{3+}$ ion is a much superior promoter than $H^+$ ion and comparison of $\Delta S^{\neq}$ values indicates that this is chiefly due to a more favourable entropy effect. For the $Fe^{3+}$ catalysed dissociation of all the three complexes a plot of $\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ is linear; this iso-kinetic relation indicates a similar mechanism. The plots of log $k_M$ for the $[Co(ox)_3]^{3-}$ system[5] *vs* log $k_M$ for $[Cr(ox)_3]^{3-}$ (Figure 2A) and log $k_M$ for dissociation[3,4] of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ *vs* log $k_M$ for $[Cr(ox)_3]^{3-}$ (Figure 2B) are also linear.

TABLE I

Second order rate constants ($10^4 k_M$, $M^{-1} sec^{-1}$) for the catalysed dissociatoin of $[Cr(ox)_3]^{3-}$.

| Temp. (°C) | $Fe^{3+a}$ | $Cu^{2+b}$ | $Ni^{2+b}$ | $Zn^{2+b}$ | $Co^{2+b}$ | $Mn^{2+b}$ | $H^{+c}$ |
|---|---|---|---|---|---|---|---|
| 20 | 288 ± 15 | | | | | | |
| 25 | 567 ± 15 | 10.33[d] | 0.35[d] | 0.18[d] | 0.126[d] | 0.022[d] | 0.162[d] |
| 30 | 1088 ± 26 | 19.2 ± 0.5 | | | | | |
| 35 | | 32.0 ± 0.5 | | | | | |
| 40 | | 63.8 ± 2.2 | | | | | |
| 50 | | | 6.67 ± 0.5 | | | | |
| 60 | | | 17.50 ± 0.3 | 10.5 ± 0.3 | 5.83 ± 0.5 | | |
| 70 | | | | 25.3 ± 0.3 | 14.83 ± 0.67 | 2.98 ± 0.02 | |
| 80 | | | 117.6 ± 1.7 | 55.7 ± 2.3 | 40.67 ± 0.67 | 6.38 ± 0.35 | |
| 90 | | | | | | 18.50 ± 0.17 | |
| $\Delta H^{\neq}$ (kJ $mol^{-1}$) | 95.4 ± 3.5 | 90.3 ± 5.4 | 89.9 ± 0.8 | 90.3 ± 0.8 | 90.3 ± 3.8 | 90.3 ± 1.7 | 90.3 |
| $\Delta S^{\neq}$ ($JK^{-1}$ $mol^{-1}$) | 50.2 ± 11.7 | –0.4 ± 18.4 | –30.1 ± 2.5 | –34.3 ± 2.5 | –37.2 ± 10.9 | –51.8 ± 5.0 | –35.1 |

[a] [Complex], 1 × $10^{-4}$ M; $[H^+]$, 0.2 M; $[Fe^{3+}]$, (1-8) × $10^{-3}$ M; I, 1.0 M. [b] [Complex], 2 × $10^{-3}$ M; $[H^+]$, 0.02 M; $[M^{2+}]$, 0.02-0.25 M; I, 1.0 M. [c] Ref. 10. [d] Calculated values.

TABLE II
Second order rate constants ($k_M$, $M^{-1}$ $sec^{-1}$) for catalysed dissociation of the complexes.

| Temp. (°C) | $[Cr(ox)(H_2O)_4]^+$ | | *cis*-$[Cr(ox)_2(OH_2)_2]^-$ | |
|---|---|---|---|---|
| | $M^{n+} = Fe^{3+a}$ | $M^{n+b}$ | $M^{n+} = Fe^{3+c}$ | $M^{n+} = H^{+d}$ |
| 25[e] | $2.68 \times 10^{-7}$ | $1.95 \times 10^{-9}$ | $1.03 \times 10^{-3}$ | $2.4 \times 10^{-6}$ |
| 75 | $(2.25 \pm 0.13) \times 10^{-4}$ | | | |
| 80 | $(4.00 \pm 0.20) \times 10^{-4}$ | | | |
| 85 | $(7.00 \pm 0.20) \times 10^{-4}$ | | | |
| 90 | $(11.67 \pm 0.25) \times 10^{-4}$ | | | |
| $\Delta H^{\neq}$ (kJ $mol^{-1}$) | 1136 ± 0.5 | 99.9[f] | 101.2 ± 2.1 | 99.9[f] |
| $\Delta S^{\neq}$ ($JK^{-1}$ $mol^{-1}$) | 9.2 ± 1.4 | −75.7[f] | 37.2 ± 6.7 | −18.8[f] |

[a] This work; [Complex], $2 \times 10^{-3}$ M; $[H^+]$, 1.0 M; $[Fe^{3+}]$, $(2\text{–}6) \times 10^{-2}$ M; I, 2 M. [b] Ref. 9. [c] Ref. 4; $[Complex]_T = 0.10$ $[Fe^{3+}]$; $[H^+]$, 0.04–0.9 M; $[Fe^{3+}]$, $0.77\text{–}7.96 \times 10^{-3}$ M; I = 1 M. [d] Ref. 13. [e] Calculated values. [f] Standard deviations not reported.

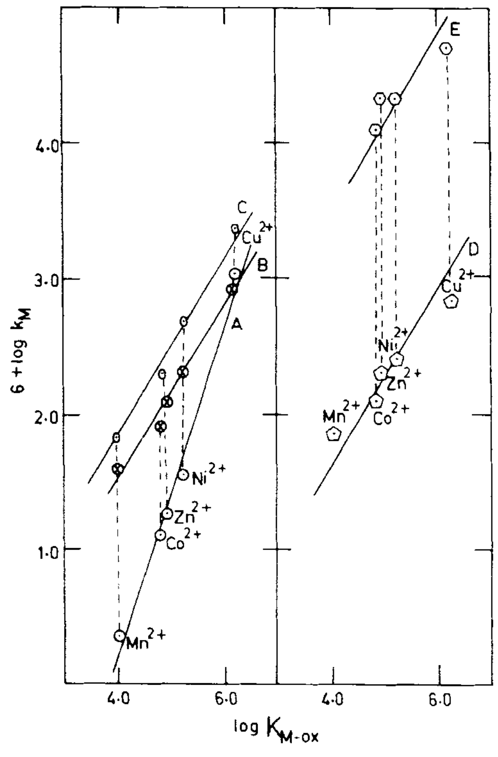

FIGURE 1 (A) Dissociation of $Cr(ox)_3^{3-}$ at 25° (slope = 1.32) (This work); (B) Dissociation of $[Co(ox)_3]^{3-}$ at 32.5° (slope = 0.65) (Ref. 5); (C) Dissociation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ at 60° (slope = 0.66) (Ref. 3); (D) Racemization of $[Cr(ox)_3]^{3-}$ at 25° (slope = 0.63) (Ref. 14); (E) Isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ (slope = 0.62) (Ref. 15).

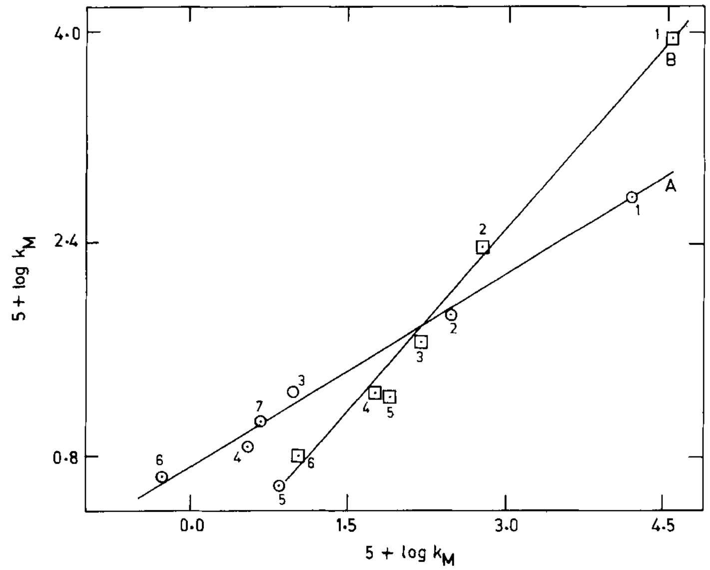

FIGURE 2 (A) log $k_M$ for $[Co(ox)_3]^{3-}$ (Ref. 5) *vs* log $k_M$ for $[Cr(ox)_3]^{3-}$ (this work) at 32.5°; (B) log $k_M$ for *cis*-$[Cr(ox)_2(OH_2)_2]^-$ (Ref. 3, 4) *vs* log $k_M$ for $[Cr(ox)_3]^{3-}$ (this work) at 60°: (1) $Fe^{3+}$; (2) $Cu^{2+}$; (3) $Ni^{2+}$; (4) $Co^{2+}$; (5) $H^+$; (6) $Mn^{2+}$; (7) $Zn^{2+}$.

Based on these observations it may reasonably be postulated that the dissociation of the substrate complex RL, in the presence of the catalysing metal ion M, proceeds through the sequence (*3*).

$$RL + M \overset{K_{MLR}}{\rightleftharpoons} RLM \xrightarrow{k_{MLR}} R + LM \qquad (3)$$

The fact that $Fe^{3+}$ exhibits a marked catalytic activity even in the case of the cationic complex $[Cr(ox)(OH_2)_4]^+$ suggests that the intermediate RLM is not a mere ion-pair but that it involves specific bonding interaction presumably through the Cr(III) bound oxalate functioning as a bridging chelating ligand to bind the $Fe^{3+}$ through both the free carbonyl oxygens. Direct evidence of such a chelated bridging exalate has been furnished in the case of $[\{Ni(en)_2\}_2(C_2O_4)](NO_3)_2$ on the basis of IR and X-ray data.[16]

Based on (*3*) we get, under conditions that the concentration of RLM is negligible compared to RL, the relation (*4*). From (*4*) and the known fact[17] that log of formation constants of complexes of two similar ligands (log $K_{MLR}$ and log $K_{ML}$ corresponding to the ligands RL and L in the present cases) with a series of metal ions is linearly related (see Figure 3) it can be shown that the plot of log $k_M$ *vs* log $K_{ML}$ will be linear. Analysis of literature data and the data from the present work amply substantiates this prediction (see Figure 1) and is in support of the proposed mechanism.

$$k_M = K_{MLR} \bullet k'_{MLR} \qquad (4)$$

Dissociations of the $[Cr(ox)_3]^{3-}$ complex catalysed by different electrophiles including $H^+$ are practically iso-enthalpic (see Table I) and the relative catalytic activity is due chiefly to an entropy effect. This is what has previously been observed for a number of similar reactions of oxalato complexes of Cr(III)[4,11,22] and Co(III)[5,19] The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values (see Table II) for the acid and $Fe^{3+}$ catalysed dissociations of [Cr(ox)

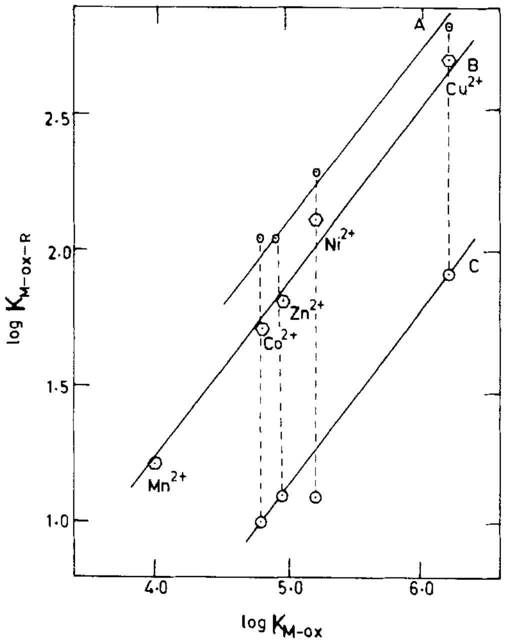

FIGURE 3 R = $[Co(NH_3)_5]^{3+}$ (A) (slope 0.66) (Ref. 18); $[Co(en)_2(NH_3)]^{3+}$ (B) (slope = 0.60) (Ref. 19); $C_2H_5$ (C) (slope 0.64) (Ref. 20).

$(OH_2)_4]^+$ indicate that for these reactions also the relative rates are entropy controlled. A plot of $(\Delta S^{\neq})$ *vs* log $K_{M-ox}$ is linear for the catalysed dissociation of $[Cr(ox)_3]^{3-}$ (see Figure 4B), and similar behaviour is found for the racemization[21] of $[Cr(ox)_3]^{3-}$ (see Figure 4A).

For a given metal ion (say $Fe^{3+}$), the catalytic activity as well as the entropy of activation follows the sequence $[Cr(ox)_3]^{3-} > [Cr(ox)_2(OH_2)_2]^- > [Cr_2(ox)(OH_2)_4]^+$, while

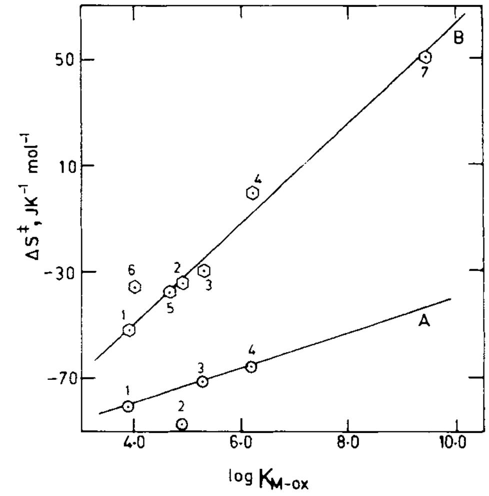

FIGURE 4 (A) Racemization of $[Cr(ox)_3]^{3-}$ (Ref. 21); (B) Dissociation of $[Cr(ox)_3]^{3-}$ (this work): (1) $Mn^{2+}$; (2) $Zn^{2+}$; (3) $Ni^{2+}$; (4) $Cu^{2+}$; (5) $Co^{2+}$; (6) $H^+$; (7) $Fe^{3+}$.

the enthalpy of activation changes in the opposite sense. Complexation of $M^{n+}$ should obviously be strongest with the *tris*- and weakest with the *mono*-oxalato complex, the *bis*-complex occupying an intermediate position. Based on considerations of the extent of charge neutralisation in the intereaction of $M^{n+}$ with each of the three oxalato complexes one expects the degree of desolvation to follow the sequence $[Cr(ox)_3]^{3-} > [Cr(ox)_2(OH_2)_2]^- > [Cr(ox)(OH_2)_4]^+$ thus accounting for the observed trend in $\Delta S^{\neq}$ values.

## ACKNOWLEDGEMENT

This investigation was carried out with financial assistance from the CSIR, New Delhi, for which the award of a post-doctoral research fellowship to one of us (R.N.B.) are also thankfully acknowledged.

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