

## Kinetics of the Oxidation of [*N*-(2-Hydroxyethyl)ethylenediamine-*N,N',N'*-triacetato]chromium(III) by Periodate

Ahmed A. ABDEL-KHALEK\* and Mahmoud M. ELSEMONGY†

Chemistry Department, Faculty of Science, Cairo University, Beni-Suef City, Egypt

†Chemistry Department, Faculty of Education, Umm Al-Qura University, Al-Taif City, Shihar, Saudi Arabia  
(Received November 19, 1987)

The kinetics of oxidation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ , ( $\text{TOH} = N$ -(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetate) by periodate in aqueous solutions has been found to obey the following equation

$$\text{Rate} = \frac{k_2 K_6 [\text{Cr}^{\text{III}}]_{\text{T}} [\text{I}^{\text{VII}}]_{\text{T}}}{1 + [\text{H}^+]/K_5 + K_6 [\text{I}^{\text{VII}}]_{\text{T}}}$$

where  $k_2$  is the rate constant for the electron-transfer process,  $K_5$  is the equilibrium constant for dissociation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$  to  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})]^- + \text{H}^+$  and  $K_6$  is the pre-equilibrium formation constant. The activation parameters are reported. It is proposed that electron transfer proceeds via an inner-sphere mechanism with the hydroxo ligand of the chromium(III) complex bridging the two reactants.

Metal complexes, which are relatively easily oxidized by  $\text{IO}_4^-$  in aqueous solution, seem to fall into one of two classes: (i) labile complexes<sup>1-6</sup> or (ii) inert complexes that can offer a bridging ligand.<sup>7,8</sup> The mechanism of oxidation of the labile complexes is believed to be of the inner-sphere type, and in several cases direct evidence in support of this mechanism has been presented.<sup>2-6</sup> Substitution into the inner coordination sphere of the  $\text{IO}_4^-$  ion, which is labile, is likely.<sup>9</sup> In case of oxidation of  $[\text{Cr}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]$  by periodate,<sup>6</sup> it was proposed that the oxidation may proceed via one- or two-electron transfer giving Cr(IV) or Cr(V), respectively, in the rate-determining step, followed by a fast step leading to Cr(VI). An inner-sphere process is also believed to be operating in the oxidation of inert complexes.<sup>7,8</sup> The unusual second-order dependence on  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  in the chromium(III)-periodate reaction seems to support an inner-sphere mechanism.<sup>7</sup> The two electron transfer step proposed for this reaction requires this mechanism,<sup>10</sup> where the hydroxo form,  $[\text{CrOH}]^{2+}$ , was considered to be the reactive chromium(III) species.

In particular we have chosen the edta analogues in that it can be supported that some properties of the respective complexes are influenced by the position and number of the functional groups. In this study the kinetics of oxidation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ , where TOH is *N*-(2-hydroxyethyl)ethylenediaminetriacetate, is reported.

### Experimental

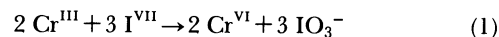
**Reagents.** Reagent grade *N*-(2-hydroxyethyl)ethylenediamine-*N,N',N'*-triacetic acid, sodium periodate, chromium(III) nitrate hexahydrate, sodium dihydrogenphosphate, sodium hydroxide, and sodium nitrate were used without further purification. Solution of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$  was prepared by the method of Wharton and Sykes.<sup>11</sup> Molar absorption coefficients of this complex were calculated on the basis of the chromium concentration which was determined spectrophotometrically as chromate.<sup>12</sup> At the range

of pH 6.1–7.3 the species found in the solution have  $\epsilon_{394} = 104$  and  $\epsilon_{575} = 133 \text{ M}^{-1} \text{ cm}^{-1}$  ( $\text{M} = \text{mol dm}^{-3}$ ) as reported for  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})]^-$ .<sup>11</sup> A stock solution of periodate was made up by weight and wrapped with Al foil to avoid photochemical decomposition.<sup>13</sup> Sodium dihydrogenphosphate, sodium hydroxide, and sodium nitrate solutions were made up by weight. Buffer solutions were made up from sodium dihydrogenphosphate-sodium hydroxide mixtures.

**Kinetic Measurements.** A Unicam SP8000 spectrophotometer, equipped with a thermostated cell holder, was used to monitor the reaction. The reactants in buffer solutions in the two compartments of an intended flask, were thermostated for about 20 minutes. These were thoroughly mixed and quickly transferred to an absorption cell. The formation of the chromium(VI) was followed at a wavelength in the 350–372 nm range where the absorption is maximal at the pH of the reaction. Pseudo-first order conditions were maintained in all runs by using a large excess of periodate concentrations (more than 10-fold) over those of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ . The pH of the reaction was measured on a Radiometer digital pH meter model PHM62. The ionic strength was maintained constant by using the appropriate amounts of sodium nitrate solution.

### Results and Discussion

The stoichiometry of the  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})] - \text{IO}_4^-$  reaction can be represented by Eq. 1



where  $\text{Cr}^{\text{III}}$  and  $\text{I}^{\text{VII}}$  represent total chromium(III) and periodate, respectively. The concentration ratio of  $\text{IO}_4^-$  initially present to  $\text{Cr}^{\text{VI}}$  produced was found to be  $1.50 \pm 0.04$ . The stoichiometry is also consistent with the observation that  $\text{IO}_3^-$  does not oxidize the chromium(III) complex over the pH range where the kinetics was investigated.

At all the chromium(III) complex concentrations used, in presence of vast excess of periodate, plots of  $\ln(A_\infty - A_t)$  vs. time, where  $A_\infty$  and  $A_t$  are the absorbances at infinity and time  $t$ , respectively, were linear up to 85% of the reaction. The pseudo-first order rate con-

Table 1. Dependence of the  $\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})/\text{IO}_4^-$  Reaction Rate on  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ ,  $[\text{IO}_4^-]$  at  $\text{pH}=7.30$  and  $I=0.5\text{ M}$ ,<sup>a</sup> at Different Temperatures

| $T$                | $10^2[\text{IO}_4^-]$ | $10^4 k_{\text{obs}}$       |
|--------------------|-----------------------|-----------------------------|
| $^{\circ}\text{C}$ | M                     | $\text{s}^{-1}$             |
| 20                 | 0.2                   | $8.05 \pm 0.12$             |
| 20                 | 0.3                   | $10.00 \pm 0.20$            |
| 20                 | 0.5                   | $11.60 \pm 0.25$            |
| 20                 | 1.0                   | $12.80 \pm 0.31$            |
| 20                 | 2.0                   | $13.90 \pm 0.40$            |
| 25                 | 0.5                   | $20.80 \pm 0.60$            |
| 25                 | 1.0                   | $24.20 \pm 0.70$            |
| 25                 | 2.0                   | $26.30 \pm 0.83$            |
| 25                 | 2.0                   | $26.40 \pm 0.75^{\text{b}}$ |
| 25                 | 2.0                   | $26.25 \pm 0.80^{\text{c}}$ |
| 25                 | 2.0                   | $26.37 \pm 0.77^{\text{d}}$ |
| 25                 | 3.0                   | $27.02 \pm 0.79$            |
| 25                 | 4.0                   | $27.39 \pm 0.85$            |
| 25                 | 5.0                   | $27.77 \pm 0.80$            |
| 30                 | 0.2                   | $20.80 \pm 0.64$            |
| 30                 | 0.3                   | $25.00 \pm 0.81$            |
| 30                 | 0.5                   | $29.40 \pm 0.90$            |
| 30                 | 1.0                   | $36.60 \pm 1.20$            |
| 30                 | 2.0                   | $40.50 \pm 1.34$            |
| 35                 | 0.5                   | $42.60 \pm 1.28$            |
| 35                 | 1.0                   | $52.60 \pm 1.40$            |
| 35                 | 2.0                   | $60.61 \pm 1.43$            |
| 35                 | 3.0                   | $65.32 \pm 1.50$            |
| 35                 | 5.0                   | $66.70 \pm 1.49$            |

a) Unless otherwise stated  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]=1.0 \times 10^{-4}\text{ M}$ . For b), c), and d),  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$  was  $2.0 \times 10^{-5}\text{ M}$ ,  $5 \times 10^{-5}\text{ M}$ , and  $2.0 \times 10^{-4}\text{ M}$  respectively.

stant,  $k_{\text{obs}}$ , was calculated from the slopes of these plots by using a linear least-squares program.

The constancy of  $k_{\text{obs}}$ , over the complex concentration range  $(5.0\text{--}20.0) \times 10^{-4}\text{ M}$  under the fixed experimental conditions, shown in Table 1, is in agreement with a first-order dependence on its concentration.

The variation of  $k_{\text{obs}}$  with periodate concentration, Table 1, exhibits rate saturation at high periodate. Plots of  $1/k_{\text{obs}}$  versus  $1/[\text{IO}_4^-]$  were found to be linear with a definite intercept as shown in Fig. 1. The dependence of  $k_{\text{obs}}$  on periodate concentration is thus described by

$$k_{\text{obs}} = \frac{a[\text{IO}_4^-]}{1 + b[\text{IO}_4^-]} \quad (2)$$

or

$$1/k_{\text{obs}} = \frac{1}{a[\text{IO}_4^-]} + \frac{b}{a} \quad (3)$$

The values of  $a$  and  $b$  were obtained from the slope and the intercept as  $(1.52 \pm 0.6)\text{ M}^{-1}\text{ s}^{-1}$  and  $(529 \pm 15)\text{ M}^{-1}$ , respectively at  $25^{\circ}\text{C}$  and  $\text{pH}=7.30$ .

The effect of hydrogen-ion concentration on the reaction rate was investigated over the  $\text{pH}$  range  $6.10\text{--}7.30$ . Table 2 shows that the rate of reaction increases with increasing  $\text{pH}$  value.

Table 2. Effect of  $\text{pH}$  on  $k_{\text{obs}} (\text{s}^{-1})$  at  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]=1.0 \times 10^{-4}\text{ M}$ ,  $I=0.5\text{ M}$ , and  $T=25^{\circ}\text{C}$

| $10^2[\text{IO}_4^-]$ | $10^4 k_{\text{obs}}/\text{s}^{-1}$ |                  |                  |                  |
|-----------------------|-------------------------------------|------------------|------------------|------------------|
| M                     | $\text{pH}=7.30$                    | $\text{pH}=6.91$ | $\text{pH}=6.56$ | $\text{pH}=6.10$ |
| 0.5                   | $20.80 \pm 0.60$                    | $19.23 \pm 0.50$ | $16.95 \pm 0.31$ | $12.61 \pm 0.60$ |
| 1.0                   | $24.20 \pm 0.70$                    | $22.98 \pm 0.61$ | $21.74 \pm 0.42$ | $17.40 \pm 0.56$ |
| 2.0                   | $26.30 \pm 0.83$                    | $25.77 \pm 0.55$ | $24.39 \pm 0.52$ | $21.73 \pm 0.47$ |
| 3.0                   | $27.02 \pm 0.77$                    | $26.81 \pm 0.66$ | $25.64 \pm 0.60$ | $24.11 \pm 0.63$ |
| 5.0                   | $27.77 \pm 0.80$                    | $27.25 \pm 0.75$ | $26.67 \pm 0.81$ | $25.60 \pm 0.71$ |

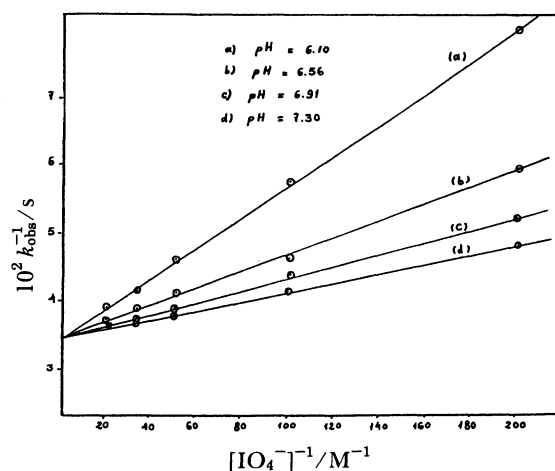
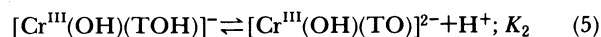
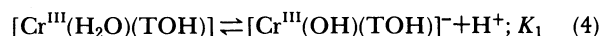


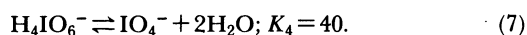
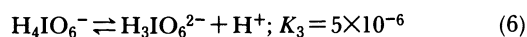
Fig. 1. Plots of  $k_{\text{obs}}^{-1}$  against  $[\text{IO}_4^-]^{-1}$ .

Bustin and Earley<sup>14</sup> reported that  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$  undergoes the following equilibria



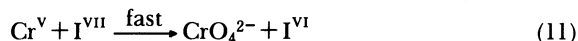
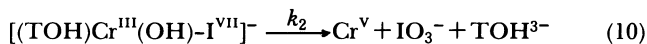
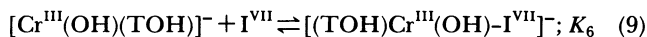
with  $K_1$  and  $K_2$  having values of  $3.63 \times 10^{-7}\text{ M}$  and  $1.58 \times 10^{-10}\text{ M}$ , respectively at  $25^{\circ}\text{C}$  and  $I=0.1\text{ M}$ . It is clear from the value of  $K_2$  that  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TO})]^{2-}$  was not present at the employed  $\text{pH}$  values at the present study. The species present at low  $\text{pH}$  has the ligand bound in a quinquedentate manner, with the 2-hydroxyethyl group uncoordinated.<sup>14</sup> The absence of an acid dissociation constant at  $\text{p}K_a$  ca. 3 precludes the presence of any uncomplexed- $\text{COO}^-$  groups.<sup>14</sup>

From the reported equilibrium constants of aqueous periodate solutions, it may be concluded that, over the  $\text{H}^+$  range used in this study, the periodate species likely to be present are  $\text{IO}_4^-$ ,  $\text{H}_4\text{IO}_6^-$ , and  $\text{H}_3\text{IO}_6^{2-}$ <sup>15</sup> which are in the equilibria



It is clear from the value of  $K_4$  that  $\text{IO}_4^-$  is not predominant species ( $\text{I}^{\text{VII}}$  will be used to represent  $\text{H}_4\text{IO}_6^-$  and  $\text{H}_3\text{IO}_6^{2-}$ ).

The experimental rate equation suggests that a fast equilibrium step precedes the slow intramolecular electron transfer step. A possible mechanism is described by Eqs. 8—12.



From the above mechanism, rate of the reaction is given by

$$\begin{aligned} \text{rate} &= k_2[(\text{TOH})\text{Cr}^{\text{III}}(\text{OH})-\text{I}^{\text{VII}}] \\ &= k_2 K_6 [\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})^-][\text{I}^{\text{VII}}]. \end{aligned} \quad (13)$$

If  $[\text{Cr}^{\text{III}}]_{\text{T}}$  represent the total concentrations of  $\text{Cr}^{\text{III}}$  species, then

$$[\text{Cr}^{\text{III}}]_{\text{T}} = [\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})^-][\text{H}^+]/K_5 + [\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})^-] + K_6 [\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})^-][\text{I}^{\text{VII}}]. \quad (14)$$

Substitution for  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})^-]$  from Eq. 14 into Eq. 13, gives

$$\text{rate} = k_2 K_6 [\text{Cr}^{\text{III}}]_{\text{T}} [\text{I}^{\text{VII}}]_{\text{T}} / 1 + ([\text{H}^+]/K_5) + K_6 [\text{I}^{\text{VII}}]_{\text{T}} \quad (15)$$

and

$$k_{\text{obs}} = k_2 K_6 [\text{I}^{\text{VII}}]_{\text{T}} / 1 + ([\text{H}^+]/K_5) + K_6 [\text{I}^{\text{VII}}]_{\text{T}} \quad (16)$$

which on rearrangement, gives

$$1/k_{\text{obs}} = K_5 + [\text{H}^+]/k_2 K_5 K_6 [\text{I}^{\text{VII}}]_{\text{T}} + 1/k_2. \quad (17)$$

At constant  $[\text{H}^+]$  Eq. 18 follows, in which  $A$  is a constant

$$1/k_{\text{obs}} = A/k_2 K_5 K_6 [\text{I}^{\text{VII}}]_{\text{T}} + 1/k_2 \quad (18)$$

which is identical to the experimental results shown in Eq. 3, where  $a = k_2 K_5 K_6 / A$  and  $b = K_5 K_6 / A$ .

Values of  $k_2$  and  $K_6$ , at the temperature used, calculated from these relationships, by substitution  $K_5 = 3.63 \times 10^{-7}$  M, are listed in Table 3. The activation parameters obtained from a least-squares' fit to the transition state theory equation are  $\Delta H^\ddagger = 76.0 \pm 2.1$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -38.7 \pm 7.1$  J K<sup>-1</sup> mol<sup>-1</sup>. The enthalpy of the pre-equilibrium reaction  $\Delta H_6^\circ = -32.1 \pm 1.7$  kJ mol<sup>-1</sup> is obtained from the temperature variation of  $K_6$ . Negative  $\Delta S^\ddagger$  for the redox reactions between reactants with charges of the same sign were claimed to be largely the result of the charge concentration on encounter complex formation, which causes substantial mutual ordering of the solvated water molecules.<sup>16)</sup> Value of  $\Delta H_6^\circ$  indicates that the formation of the precursor complex  $[(\text{TOH})\text{Cr}^{\text{III}}(\text{OH})-\text{I}^{\text{VII}}]^-$ , is an exothermic process as found in the reaction between  $[\text{Co}^{\text{II}}(\text{edta})^{2-}]$  and  $\text{IO}_4^-$ .<sup>3)</sup> The intramolecular electron transfer step, is endothermic as indicated by the value of  $\Delta H_2^\ddagger$ .

Table 3. Values of  $k_2$  and  $K_6$  at Different Temperatures

| $T/^\circ\text{C}$ | $10^3 k_2/\text{s}^{-1}$ | $K_6/\text{M}^{-1}$ |
|--------------------|--------------------------|---------------------|
| 20                 | 1.50                     | 751                 |
| 25                 | 2.95                     | 596                 |
| 30                 | 4.31                     | 503                 |
| 35                 | 7.30                     | 414                 |

The contributions of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  to the rate constant seem to compensate each other. This fact suggests that the factors controlling  $\Delta H^\ddagger$  must be closely related to those controlling  $\Delta S^\ddagger$ . Therefore, the solvation state of the encounter complex would be important in determining  $\Delta H^\ddagger$ .<sup>16)</sup> Thus, the relatively small enthalpy of activation,  $\Delta H_2^\ddagger$ , can be explained in terms of the formation of more solvated complex  $[(\text{TOH})\text{Cr}^{\text{III}}(\text{OH})-\text{I}^{\text{VII}}]^-$ .<sup>17)</sup>

From Eq. 17 and Fig. 1, it follows that slopes of the plots can be represented by Eq. 19.

$$\text{slope} = [\text{H}^+]/k_2 K_5 K_6 + 1/k_2 K_6 \quad (19)$$

It is obvious, from Eq. 19 that the slope is dependent on  $[\text{H}^+]$ . This plot is shown in Fig. 2 which indicates the validity of our proposed mechanism. Value of  $K_5$  was calculated from Fig. 2, to be  $2.70 \times 10^{-7}$  M. This value is in good agreement with the reported<sup>14)</sup> value of  $K_5 = 3.63 \times 10^{-7}$  M at 25 °C. The equilibrium constant  $K_6$  obtained from Eq. 19 and Fig. 2 is 571 M<sup>-1</sup> which is in a good agreement ( $K_6 = 596$  M<sup>-1</sup>) with that obtained from Eq. 18 and Fig. 1 at 25 °C.

An innersphere mechanism is proposed for the oxidation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]^-$  by  $\text{IO}_4^-$  in which the  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})]^-$  is bridged to  $\text{IO}_4^-$  through the hydroxo ligand because hydroxide on  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})]^-$  is a better bridging ligand than  $\text{H}_2\text{O}$  on  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ . The assignment of an inner-sphere mechanism through the hydroxo bridge for this reaction seems to be supported by the following reasons: (i) Periodate ion is capable of acting as a ligand as evidenced from its coordination to copper(III)<sup>18)</sup> and nickel(IV).<sup>19)</sup> (ii) The hydroxo ligand is a firm ligand bridge. (iii) No reaction was observed at pH below 6.0 where the hydroxo species is not present. (iv) The inverse dependence of  $[\text{H}^+]$  is usually ascribed to oxidation of the hydroxy species offering a very effective OH bridge in an innersphere process.<sup>20)</sup>

The oxidation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]^-$  by  $\text{IO}_4^-$  may proceed via one- or two-electron transfer giving  $\text{Cr}^{\text{IV}}$  or

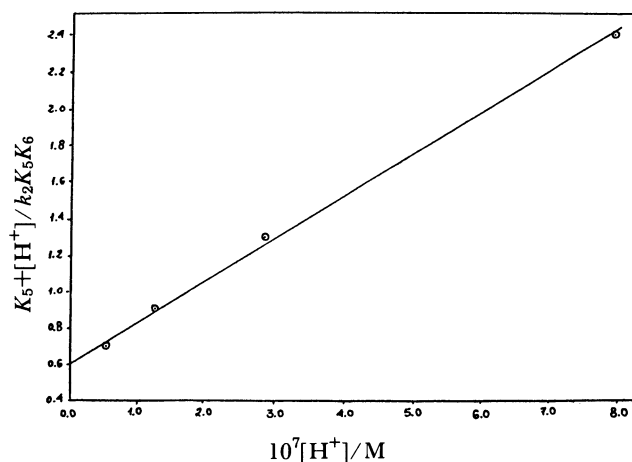


Fig. 2. Plots of  $K_5 + [\text{H}^+] / k_2 K_5 K_6$  vs.  $[\text{H}^+]$ .

$\text{Cr}^{\text{V}}$ , respectively in the rate determining step. These may then followed by a fast step leading to  $\text{Cr}^{\text{VI}}$ . The fact that acrylonitrile was not polymerized seems to support two-electron transfer process.

In comparison with oxidation of  $[\text{Cr}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]$ ,<sup>7)</sup> under the same conditions, the both hydroxy complexes,  $[\text{Cr}^{\text{III}}(\text{edta})(\text{OH})]^{2-}$  and  $[\text{Cr}^{\text{III}}(\text{OH})(\text{TOH})]^-$ , are significantly more reactive than their conjugate acids. Value of  $k_2K_6$  ( $k_2$  is the intramolecular transfer rate constant and  $K_6$  is the pre-equilibrium formation constant), for the oxidation of  $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})(\text{TOH})]$ , is equal to 1.74 at 25 °C. This value is very close to the value of  $k^{\text{et}}K_4$  ( $1.81 \pm 0.18$ ) for the oxidation of  $[\text{Cr}^{\text{III}}(\text{edta})(\text{H}_2\text{O})]$ , where  $k^{\text{et}}K_4$  corresponds to  $k_2K_6$ . It would be more informative to compare the intramolecular electron transfer rate constants. However, this is not possible because the value of  $k^{\text{et}}$  for the edta complex is not known.

It is a great pleasure to acknowledge Prof. Y. Sulfab, Chemistry Department, Faculty of Science, Kuwait University, for his useful ideas.

#### References

- 1) Y. Sulfab and A. I. Abu-Shadi, *Inorg. Chim. Acta*, **21**, 115 (1977).
- 2) A. Y. Kasim and Y. Sulfab, *Inorg. Chim. Acta*, **24**, 247 (1977).
- 3) F. R. El-Eziri and Y. Sulfab, *Inorg. Chim. Acta*, **25**, 15 (1977).
- 4) A. A. Abdel-Khalek and Y. Sulfab, *J. Inorg. Nucl. Chem.*, **43**, 3257 (1981).
- 5) M. A. Hussein, A. A. Abdel-Khalek, and Y. Sulfab, *J. Chem. Soc., Dalton Trans.*, **1983**, 317.
- 6) N. A. Al-Jallal and Y. Sulfab, *Transition Met. Chem.*, **8**, 51 (1983).
- 7) A. Y. Kasim and Y. Sulfab, *Inorg. Chem.*, **20**, 506 (1981).
- 8) P. Guardado, A. Maestra, and M. Baton, *J. Inorg. Nucl. Chem.*, **43**, 1392 (1981).
- 9) I. Pechet and Z. Luz, *J. Am. Chem. Soc.*, **87**, 4086 (1965).
- 10) R. Buchacek and G. Gordon, *Inorg. Chem.*, **11**, 2154 (1972).
- 11) R. K. Wharton and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, **1972**, 2404.
- 12) G. W. Haupt, *J. Res. Natl. Bur. Stand. (U.S.)*, **48**, 414 (1952).
- 13) M. C. R. Symon, *J. Chem. Soc.*, **1955**, 2794.
- 14) D. I. Bustin and J. E. Earley, *J. Am. Chem. Soc.*, **89**, 1818 (1967).
- 15) S. H. Laurie, J. M. Williams and C. J. Nyman, *J. Phys. Chem.*, **68**, 1311 (1964).
- 16) M. J. Weaver and E. L. Yee, *Inorg. Chem.*, **19**, 1936 (1980).
- 17) Y. Sasaki and R. Kawamura, *Bull. Chem. Soc. Jpn.*, **54**, 3379 (1981).
- 18) I. Hadinec, L. Jenovsky, A. Linek, and V. Synecek, *Naturwiss.*, **47**, 377 (1960).
- 19) P. Ray, *Inorg. Synth.*, **5**, 201 (1957).
- 20) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes," Allyn & Bacon, Boston (1970), p. 262.