

# Kinetics and mechanism of hexachloroiridate(IV) oxidation of tellurium(IV) in aqueous solutions

Cite this: *New J. Chem.*, 2013, **37**, 2700

Refat Hassan,<sup>a</sup> Ishaq Zaafarany,<sup>b</sup> Hideo Takagi<sup>c</sup> and Yasuhisa Ikeda<sup>d</sup>

The kinetics of oxidation of tellurium(IV) by  $[\text{IrCl}_6]^{2-}$  in aqueous perchlorate solutions at a constant ionic strength of  $0.1 \text{ mol dm}^{-3}$  have been investigated spectrophotometrically. The results showed a first-order dependence in  $[\text{IrCl}_6]^{2-}$ , fractional-first-order kinetics with respect to tellurium(IV) concentration and second-order overall kinetics. The increase in the  $[\text{H}^+]$  was found to be accompanied by a decrease in the rate constants, i.e., the oxidation reaction was acid-inhibited. Kinetic evidence for the formation of a 1 : 1 intermediate binuclear complex between the two reactants has been obtained. The ionization constant of tellurium(IV) has been evaluated and found to be  $1.69 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$  at  $25^\circ\text{C}$ . The kinetic parameters have been calculated and a tentative reaction mechanism consistent with the kinetic data is suggested.

Received (in Montpellier, France)  
9th April 2013,  
Accepted 5th June 2013

DOI: 10.1039/c3nj00373f

[www.rsc.org/njc](http://www.rsc.org/njc)

## Introduction

Tellurium(IV) is used in the manufacture of colored glasses, in ceramics, enamel pigments and as bases for phosphors. It is also used as a secondary vulcanizing agent for natural rubber and as an oxidation inhibitor in lubricating oil.<sup>1</sup> Some kinetic studies have reported on the oxidation of tellurium(IV) by cerium,<sup>2</sup> manganese(III)<sup>3</sup> and cobalt(III)<sup>4</sup> as one-equivalent oxidants, but the kinetics were found to be quite different in these redox systems and, hence, the reaction mechanism for the electron-transfer process still remains controversial.

The mechanistic interest of hexachloroiridate(IV) as a one-equivalent oxidant began with the inception of chemical kinetics as a tool for studying oxidation reactions, which is owed its ability to undergo a variety of oxidation mechanisms that depend on the nature of reductant. Therefore, numerous investigators have used this oxidant for studying the kinetics of the oxidation of many organic<sup>5–9</sup> and inorganic<sup>10–17</sup> substrates. However, it seems that no attempt has been made to study the oxidation of Te(IV) by hexachloroiridate(IV) as a one-equivalent oxidant. This fact may be attributed to the complexity of the

kinetics that may arise from the existence of different species of tellurium(IV) ions in aqueous solutions, which depends on the pH of the medium,<sup>2,18,19</sup> along with the formation of unstable Te(V) during the oxidation of Te(IV) to its final stable hexavalent oxidation state. The combination of all these aspects gives rise to systems of considerable complexity.

In view of the above arguments and our interest on studying the kinetics of the oxidation of 2-equiv. inorganic substrates, such as uranium(IV),<sup>10</sup> tin(II)<sup>11</sup> and arsenic(III),<sup>12</sup> by this oxidant, the oxidation of tellurium(IV) as a two-equivalent reductant by iridium(IV) seems to merit an investigation with the aim of shedding more light on the mechanism of oxidation in terms of the electron-transfer nature. The present oxidation was thought to be a useful test of the postulate that a metal–ligand transfer occurs if the oxidant is inert, which supplies a bridging ligand, and if the reducing agent is substitution labile or it expands its coordination sphere upon oxidation. In addition, this study aims to kinetically determine the hydrolysis constant of tellurium(IV).

## Experimental

### Materials

Sodium hexachloroiridate(IV) of AnalaR quality (Ventron Crop.) was used without further purification. Solutions of the reagent were freshly prepared before each experiment to minimize the influence of the rate of aquation of formed labile hexachloroiridate(III).<sup>20,21</sup> Optical density *versus* concentration plots for acidified  $[\text{IrCl}_6]^{2-}$  showed that Beer's law is obeyed at wavelengths of 418 and 489 nm and the molar extinction

<sup>a</sup> Chemistry Department, Faculty of Sciences, Assiut University, Assiut, 71516 Egypt. E-mail: rmhassan2002@yahoo.com

<sup>b</sup> Chemistry Department, Faculty of Applied Sciences, Umm Al-Qura University, Makkah Al-Mukarramah 13401, Saudi Arabia. E-mail: ishaq\_zaafarany@yahoo.com

<sup>c</sup> Chemistry Department, School of Science, Research Center for Physical Inorganic Science, Nagoya 464-01, Japan. E-mail: h.d.takagi@nagoya-u.jp

<sup>d</sup> Department of Nuclear Engineering, Tokyo Institute of Technology, Tokyo 152-8550, Japan. E-mail: yiked@nr.titech.ac.jp

coefficients were found to be  $3320 \pm 16$  and  $4070 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively, which are in good agreement with the values reported previously.<sup>10–13</sup>

Tellurium(IV) solutions were freshly prepared by dissolving sodium tellurite (BDH) in doubly distilled water or in  $\text{HClO}_4$  as required before each experiment and were standardized as described elsewhere.<sup>3,4,22</sup>

The reagent solutions were deoxygenated by passing a current of nitrogen gas through them before use in the experiments.

Doubly distilled conductively water was used in all preparations. The temperature was controlled within  $\pm 0.05^\circ\text{C}$ .

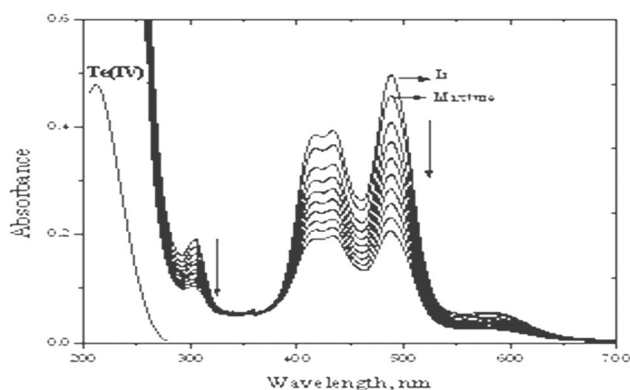
The ionic strength of the reaction mixtures was maintained at a constant  $0.1 \text{ mol dm}^{-3}$  using  $\text{NaClO}_4$  as a non-complexing agent.

All other reagents employed in the present work were of analytical grade (BDH) and their solutions were prepared by dissolving the requisite amounts of the sample in doubly distilled water.

### Kinetic measurements

Preliminary experiments indicated that the initial part of the reaction ( $\sim 5\%$ ) was too fast to be followed by the conventional spectrophotometer used. All kinetic measurements were performed under pseudo-first-order conditions where tellurium(IV) was present in a large excess over that of the  $[\text{IrCl}_6]^{2-}$  concentration, as described elsewhere.<sup>7–9</sup> The course of the reaction was followed by recording the decrease in absorbance of  $[\text{IrCl}_6]^{2-}$  at its absorption maximum, 489 nm, as a function of time. It was verified that there was no interference from other reagents at this wavelength. The absorption spectra of the reactants and typical traces of the spectral changes are shown in Fig. 1.

Some kinetic runs were carried out under second-order conditions where  $[\text{Te}^{\text{IV}}] \geq [\text{IrCl}_6]^{2-}$  to check the reproducibility of the pseudo-first-order kinetic data. The results were found to be in good agreement with each other within the experimental errors which indicates the reproducibility of the pseudo-first-order kinetic measurements.



**Fig. 1** Spectral changes in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{\text{IV}}] = 2.5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$ . Scanning time interval = 1 min.

### Polymerization test

The possibility of the formation of free radicals was examined by adding 10% (v/v) acrylonitrile to the partially oxidized reaction mixture. No precipitation was observed after a long time, which indicated the absence of free-radical intervention.

## Results

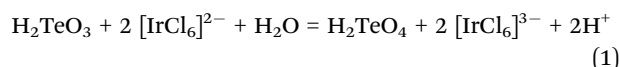
### Tellurium(IV) species

The species of tellurium(IV) are mainly dependent on the concentration of  $\text{Te}^{\text{IV}}$  and the pH of the medium.<sup>2,18,19,23–27</sup> Therefore, many forms of tellurium(IV) species exist in aqueous solutions, namely  $\text{Te}(\text{OH})_4$ ,  $\text{TiO}_3^{2-}$ ,  $\text{HTeO}_3^-$ ,  $\text{TeO}(\text{OH})_3^-$ ,  $\text{H}_2\text{TeO}_3$ ,  $\text{TeO}(\text{OH})^+$  and  $\text{Te}(\text{OH})_3^+$  species.

One should expect a homogeneous solution to be formed when one equivalent of the acid is added to the tellurium(IV) solution.<sup>26</sup> Again, since the present reaction is acid-inhibited, all experimental kinetics were maintained at relatively low acid concentrations in order to avoid the remarkable retardation of the reaction rates at higher  $[\text{H}^+]$ . Under our experimental hydrogen ion concentration, the main probable species of tellurium(IV) is  $\text{HTeO}_3^-$ .<sup>4,18,23–27</sup>

### Stoichiometry and product analysis

It is important to determine the stoichiometry coefficient of the reactants of the overall reaction since the reaction kinetics seem to be of considerable complexity. Reaction mixtures containing different initial known concentrations of the reactants with a slight excess of  $[\text{IrCl}_6]^{2-}$  in  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  of perchloric acid and  $0.1 \text{ mol dm}^{-3}$  ionic strength were equilibrated at room temperature. The unreacted iridium(IV) was estimated periodically until it reached a constant value, i.e., the reaction reached completion. Spectrophotometric estimation of the unreacted oxidant revealed that 1 mol of tellurium(IV) consumed  $2 \pm 0.1$  mol of iridium(IV). Products analysis indicated the formation of tellurium(VI) and hexachloroiridate(III) as the reaction products. This result suggests that the stoichiometry of the reaction conforms to the stoichiometric equation shown in eqn (1)†



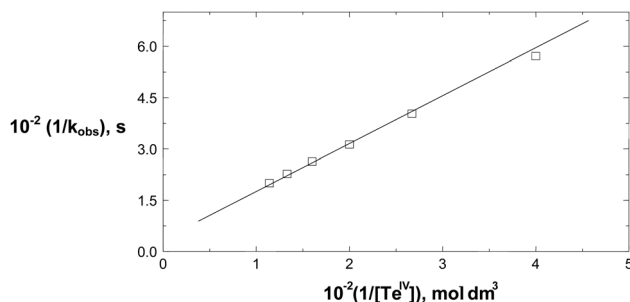
### Dependence of reaction rate on $[\text{IrCl}_6]^{2-}$ and [tellurium(IV)]

Plots of  $\log(\text{absorbance})$  vs. time were found to be linear for more than three half-lives of the reaction completion. This result indicates that the reaction is first-order with respect to  $[\text{IrCl}_6]^{2-}$ . The values of the pseudo-first-order rate constants,  $k_{\text{obs}}$ , were calculated from the gradients of these plots at a variety of initial  $[\text{IrCl}_6]^{2-}$  and tellurium(IV) concentrations. The first-order dependence was confirmed not only by the observed linearity of the pseudo-first-order plots but also by the independence of the obtained rate constants on the different initial concentrations of the oxidant ranging between

†  $\text{HTeO}_3^- + 2 [\text{IrCl}_6]^{2-} = \text{TeO}_3 + 2 [\text{IrCl}_6]^{3-} + \text{H}^+$ .

**Table 1** Pseudo-first-order and second-order rate constants in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$

$10^2 [\text{Te}^{\text{IV}}], \text{mol dm}^{-3}$	$10^3 k_{\text{obs}}, \text{s}^{-1}$	$k', \text{M}^{-1} \text{s}^{-1}$
2.50	1.65	0.70
5.00	3.20	0.64
7.50	4.40	0.59



**Fig. 2** A plot of  $1/[\text{Te}^{\text{IV}}]$  vs.  $1/k_{\text{obs}}$  in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$ .

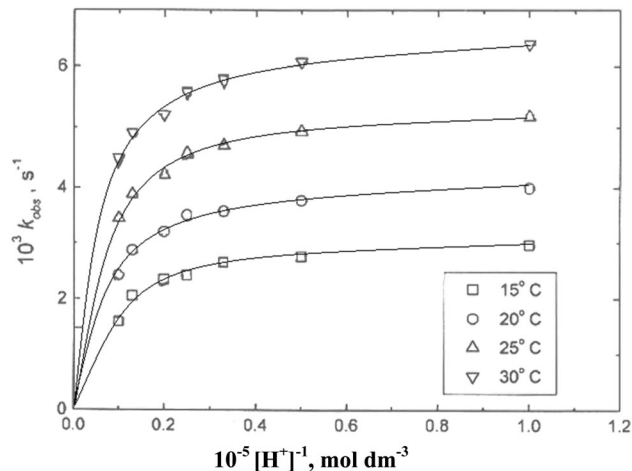
$(1-6) \times 10^{-4} \text{ mol dm}^{-3}$  in a number of steps at constant concentrations of all other reagents. The average value of  $k_{\text{obs}}$  at  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  was found to be  $5.1 \times 10^{-3} \text{ s}^{-1}$  at  $25^\circ\text{C}$ .

The non-constancy of the second-order rate constants derived from dividing the observed first-order rate constants by the initial  $[\text{Te}^{\text{IV}}]$  indicates that the rate is of fractional first-order in  $[\text{Te}^{\text{IV}}]$  as shown in Table 1. The reaction order in  $[\text{Te}^{\text{IV}}]$  was found to be  $0.95 \pm 0.1$  ( $k_{\text{obs}} = [\text{Te}^{\text{IV}}]^n$ ). Again, a plot of  $1/k_{\text{obs}}$  against  $1/[\text{Te}^{\text{IV}}]$  was found to be linear with a positive intercept on the  $1/[\text{Te}^{\text{IV}}]$  axis as shown in Fig. 2. This behavior seems to follow the Michaelis-Menten kinetics for formation of a 1:1 intermediate complex.

### Dependence of reaction rate on $[\text{H}^+]$

In order to elucidate the reaction mechanism of the present redox reaction, some kinetic measurements were performed at different  $[\text{H}^+]$  ( $10^{-4}$ – $10^{-6} \text{ mol dm}^{-3}$ ) and constants of ionic strength and temperature. An increase in acid concentration was found to be accompanied by a decrease in the observed first-order rate constants. This means that the oxidation reaction is acid-inhibited. When the observed first-order rate constants,  $k_{\text{obs}}$ , were plotted against the reciprocal of  $[\text{H}^+]$ , curvature lines passing through the origin were obtained as shown in Fig. 3.

Furthermore, some kinetic runs were performed in water in order to examine the possibility of the formation of an intermediate binuclear complex in a neutral medium as well as to check the reproducibility of the kinetic data obtained in the lower acidic solutions used. A plot of  $1/k_{\text{obs}}$  against  $1/[\text{Te}^{\text{IV}}]$  was found to be linear with a positive intercept on the  $1/k_{\text{obs}}$  axis, confirming the formation of such a binuclear complex. Again, the kinetic results obtained for the rate constants were found to



**Fig. 3** Plots of  $k_{\text{obs}}$  vs.  $1/[\text{H}^+]$  in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  at different temperatures.

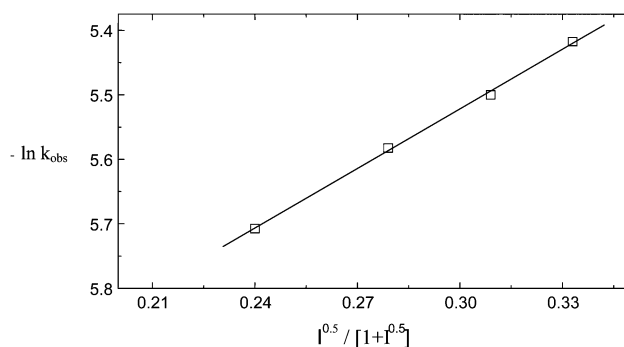
be in good agreement and with the same order of magnitude to that obtained in acidic solutions within the experimental errors. The value of  $k_{\text{obs}}$  was found to be  $5.5 \times 10^{-3} \text{ s}^{-1}$  (in  $\text{H}_2\text{O}$ ) and  $5.1 \times 10^{-3}$  (in  $0.5 \times 10^{-4} \text{ mol dm}^{-3}$  acid) at  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$  and  $25^\circ\text{C}$ .

### Dependence of reaction rate on ionic strength

In order to gain a further insight concerning the reactive species and, hence, on the mechanism of the intermediate formation, kinetic runs were performed at constants of  $[\text{H}^+]$ ,  $[\text{Te}^{\text{IV}}]$ , temperature and various of  $\text{NaClO}_4$  concentration which increased to  $0.7 \text{ mol dm}^{-3}$ . The values of  $k_{\text{obs}}$  were found to increase with increasing the ionic strength. A plot of  $\ln k_{\text{obs}}$  vs.  $I^{0.5}/(1 + I^{0.5})$  of Debye-Huckel equation was found to be linear with positive slope as shown in Fig. 4.

### Discussion

The estimated values for the relevant redox potentials of the  $\text{Te}^{\text{IV}}/\text{Te}^{\text{VI}}$  couple (0.5 V), along with the  $\text{Ir}^{\text{IV}}/\text{Ir}^{\text{III}}$  couple (0.87 V),<sup>7,28</sup> provide assurance that the stoichiometric equation defined by



**Fig. 4** Ionic strength dependence of the observed first-order rate constant in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$  and  $[\text{H}^+] = 0.5 \times 10^{-4} \text{ mol dm}^{-3}$  at  $20^\circ\text{C}$ .

eqn (1) should go to completion but offers no indication about the nature of electron-transfer mechanism.

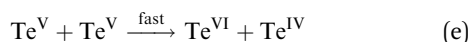
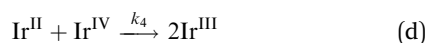
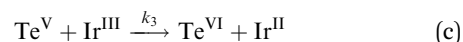
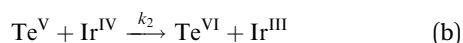
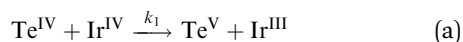
The reaction stoichiometry obtained indicates that the rate-law equation can be written as in the following relationship,

$$\text{Rate} = \frac{-d[\text{IrCl}_6]^{2-}}{dt} = 2k[\text{Te}^{\text{IV}}][\text{Ir}^{\text{IV}}] \quad (2)$$

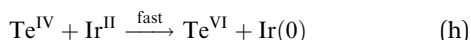
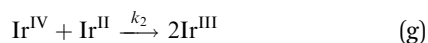
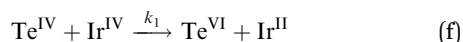
where  $k$  is the second-order rate constant.

Generally, in the oxidation of inorganic 2-equiv. reductants, such as uranium(IV),<sup>10</sup> tin(II)<sup>11</sup> and arsenic(III),<sup>12</sup> by hexachloroiridate(IV), a question of basic interest that may arise is whether the electron-transfer process proceeds *via* a successive one-electron transfer mechanism, in a sequence  $\text{M}^{\text{Z}+} \rightarrow \text{M}^{(\text{Z}-\text{e})+} \rightarrow \text{M}^{(\text{Z}-2\text{e})+}$ , or by simultaneous two-electron changes in a single step,  $\text{M}^{\text{Z}+} \rightarrow \text{M}^{(\text{Z}-2\text{e})+}$  (where  $\text{M}$  denotes the metal reductant and  $\text{Z}$  stands for its valency). The one-electron transfer mechanism may be observationally indistinguishable from two consecutive reactions of one-electron transfer steps. This problem has been reviewed by many investigators, but a detailed understanding has been limited by the lack of information on the kinetics and thermodynamics in the previously studied reactions. Hence, the knowledge on the kinetics and mechanisms of the electron-transfer nature still remains controversial and poorly understood.

Therefore, two mechanisms for the oxidation of tellurium(IV) by hexachloroiridate(IV) could be suggested here. The first one involves a one-electron transfer process in a sequence and can be represented by the following sequence of reactions (a–e):



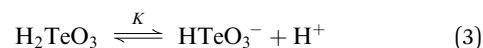
Assuming the steady-state approximation of the unstable intermediate species,  $\text{Ir}^{\text{II}}$  and  $\text{Te}^{\text{V}}$ ,<sup>9,17</sup> the rate-law expression defined by eqn (2) is obtained. The second mechanism corresponding to simultaneous two-electron changes in a single step can be defined by reactions (f–g).



This latter mechanism also leads to the rate-law expression defined by eqn (2). Therefore, both of the two above mechanisms may be considered for the oxidation in the present redox reaction.

However, the latter mechanism (reactions f–g) seems to be favorable thermodynamically. It is not favorable from the

kinetic points of view. If this mechanism operates, a precipitate of  $\text{Ir}^{\text{(0)}}$  should be observed after the reaction completion. The absence of the formation of such a precipitate after a long reaction encouraged us to exclude the two-electron transfer mechanism, but this suggestion cannot be conclusively excluded. Hence, it is more reasonable to suggest that a successive one-electron transfer mechanism occurs for the present redox reaction rather than the two-electron transfer change. The  $[\text{H}^+]$ -dependence of the rate constants may suggest the occurrence of a hydrolysis process of one of the reactants. Since, hexachloroiridate(IV) is well-known to be extremely inert for substitution (or hydrolysis),<sup>14</sup> tellurium(IV) is more likely to hydrolyze in aqueous solutions under our experimental conditions to form the more reactive species ( $\text{HTeO}_3^-$ ) prior to the rate-determining step, as in the following equilibrium,

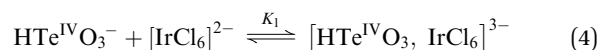


where  $K$  is the ionization constant of tellurium(IV). This suggestion may be supported by the observed protons released in the stoichiometric eqn (1). The agreement between the values of rate constants obtained in water as a neutral medium (where  $\text{HTeO}_3^-$  is the more reactive species<sup>23–27</sup>) and that in acidic media used ( $\text{pH} = 4\text{--}6$ ) may confirm the hydrolysis process defined by eqn (3).

The formation of an intermediate binuclear complex in the present reaction may be supported not only by the kinetic evidence of the Michaelis–Menten plot but also by the rapid increase of the initial absorbance of  $[\text{IrCl}_6]^{2-}$  observed in the UV-Vis region upon mixing of the oxidant with tellurium(IV), as well as the appearance of two isosbestic points at 338 and 390 nm in the spectral change as the oxidation reaction progressed (Fig. 1). Unfortunately, the initial part ( $\sim 5\%$ ) was too fast to be monitored by the conventional spectrophotometric technique used, but could hardly be considered as the rate of the oxidation of  $\text{Te}^{\text{IV}}$  by  $\text{Ir}^{\text{IV}}$  ions when considering the slowness of redox reactions involving 2-equiv. reductants by this oxidant.<sup>10–12</sup>

In view of the aforementioned aspects and the experimental observations of the  $[\text{H}^+]$  and ionic strength dependencies of the rate constants, the most reasonable reaction mechanism that can be suggested involves two competitive reactions in the rate-determining step, being  $\text{H}_2\text{TeO}_3 - [\text{IrCl}_6]^{2-}$  and  $\text{HTeO}_3^- - [\text{IrCl}_6]^{2-}$  reactions, respectively. Since, plots of  $k_{\text{obs}}$  versus  $[\text{H}^+]^{-1}$  gave curvature lines passing through the origin (Fig. 3). The first reaction that belongs to the unhydrolyzed species of tellurium(IV) is excluded. Again, the positive slope observed in the Debye–Huckel plot (Fig. 2) may indicate that the rate-determining step involves two ions of similar charges, which confirms the proposal of the second reaction mechanism.

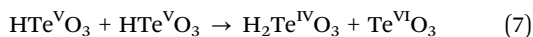
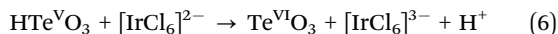
Consequently, the reaction between  $\text{HTeO}_3^-$  and  $[\text{IrCl}_6]^{2-}$  species, can be considered as the sole reaction of oxidation in the rate-determining step. It involves a rapid formation of a binuclear complex,



followed by the transfer of electrons from tellurium(IV) to iridium(IV) in the slow rate-determining step,

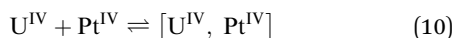
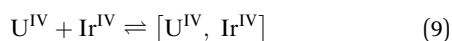
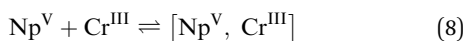


Then, the formed unstable product ( $\text{HTe}^{\text{V}}\text{O}_3$ ) is rapidly oxidized by one of the following reactions to give rise to the final oxidation product as follows

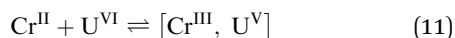


where  $K_1$  is the formation constant of complex formation and  $k$  is the rate constant of the electron transfer process.

Sullivan<sup>29</sup> and Hassan<sup>10,30</sup> reported that 1:1 binuclear complexes were formed in aqueous perchloric solutions for ( $\text{Np}^{\text{V}} - \text{Cr}^{\text{III}}$ ),<sup>29</sup> ( $\text{U}^{\text{IV}} - \text{Ir}^{\text{IV}}$ )<sup>10</sup> and ( $\text{U}^{\text{IV}} - \text{Pt}^{\text{IV}}$ ),<sup>30</sup> without the transfer of electrons as follows



On the other hand, the reduction of uranium(VI) by chromium(II)<sup>31</sup> was found to proceed *via* an intermediate binuclear complex with a simultaneous transfer of electrons from  $\text{Cr}^{\text{II}}$  to  $\text{U}^{\text{VI}}$  as defined by eqn (11),



In view of the above arguments, the main question in connection with the present redox reaction is whether the formation of the intermediate binuclear complex occurs with or without an electron-transfer process. The formation of such an intermediate is supported by the presence of  $[\text{IrCl}_6]^{2-}$  ions after the small initial rapid part, which means that there has been no reduction of iridium(IV). Considering that reaction (5) is the rate-determining step, the change of the rate constant with the change in the hydrogen ion and substrate concentrations may be expressed by eqn (12)

$$\text{Rate} = \frac{-d[\text{IrCl}_6]^{2-}}{dt} = \frac{(kKK_1[\text{H}^+]^{-1})[\text{Te}^{\text{IV}}]_{\text{T}}[\text{IrCl}_6]^{2-}}{1 + K[\text{H}^+]^{-1} + KK_1[\text{H}^+]^{-1}[\text{IrCl}_6]^{2-}} \quad (12)$$

where  $[\text{Te}^{\text{IV}}]_{\text{T}}$  is the analytical total concentration of the tellurium(IV). In the presence of a large excess of tellurium(IV) over that of  $[\text{IrCl}_6]^{2-}$ , the rate-law (12) can be rewritten as follows<sup>‡</sup>

$$\frac{1}{k_{\text{obs}}} = \left( \frac{[\text{H}^+]}{kKK_1} + \frac{1}{kK_1} \right) \frac{1}{[\text{Te}^{\text{IV}}]_{\text{T}}} + K' \quad (13)$$

According to eqn (13), at constant  $[\text{H}^+]$  a plot of  $1/k_{\text{obs}}$  vs.  $1/[\text{Te}^{\text{IV}}]$  should be a straight line, as was experimentally observed (Fig. 2). Again, plots of  $1/k_{\text{obs}}$  vs.  $[\text{H}^+]$  at constant  $[\text{Te}^{\text{IV}}]$  gave good

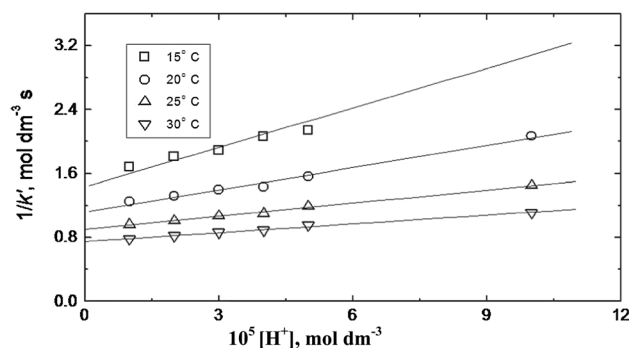
straight lines with positive intercepts on the  $1/k_{\text{obs}}$  axis. The small intercept observed in Fig. 2 may lead us to simplify eqn (13) to eqn (14), which is considered as the appropriate rate-law equation for the oxidation of tellurium(IV) by hexachloroiridate(IV).

$$\frac{[\text{Te}^{\text{IV}}]_{\text{T}}}{k_{\text{obs}}} = \frac{1}{k'_n} = \left( \frac{[\text{H}^+]}{k'} + \frac{1}{k''} \right) \quad (14)$$

where  $k'_n$  is the second-order rate constant and  $k'$  and  $k''$  are the apparent rate constants, which equal  $kKK_1$  and  $kK_1$ , respectively.

Plots of  $1/k'_n$  vs.  $[\text{H}^+]$  of eqn (14) gave good straight lines as shown in Fig. 5. From the slopes and intercepts the ionization constants and the apparent rate constants can be evaluated. These values were calculated using the least-squares method. The calculated values of the ionization constants of  $\text{Te}^{4+}$ , Table 2, were found to be in good agreement and the same order of magnitude to that reported elsewhere.<sup>26</sup>

Unfortunately, the values of the rate constant of the elementary reaction,  $k$ , could not be calculated due to the non-availability of the formation constants,  $K_1$ , at various temperatures. Some attempts have been made to evaluate the formation constants from the experimental data, but the results were unclear. Therefore, the values of the rate constants are considered to be composite quantities of the rate constants, the formation constants and the ionization constants, respectively. The activation parameters of the apparent rate constants,  $k'$  and  $k''$ , were calculated from the temperature-dependence of the rate



**Fig. 5** Plots of  $1/k'$  vs.  $[\text{H}^+]$  in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$  at different temperatures.

**Table 2** The values of ionization constants ( $K$ ) at different temperatures and the thermodynamic parameters in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{\text{IV}}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$

	Temperature (°C)			
Ionization constant	15	20	25	30
$10^3 K, \text{ dm}^3 \text{ mol}^{-1}$	0.88	1.22	1.69	2.00
Thermodynamic parameter				
$\Delta H^\circ \text{ kJ mol}^{-1}$	$\Delta S^\circ_{298} \text{ J mol}^{-1} \text{ K}^{-1}$		$\Delta G^\circ_{298} \text{ kJ mol}^{-1}$	
40.61	83.18		15.82	

<sup>‡</sup>  $K' = [\text{IrCl}_6]^{2-}/k[\text{Te}^{\text{IV}}]$ .



constants by using the method of least-squares from the Arrhenius and Eyring equations, and are summarized in Table 3. Moreover, the thermodynamic parameters of the ionization constant,  $K$ , were evaluated from well known physical methods and are listed in Table 2. The positive values observed for  $\Delta G^\circ$  and  $\Delta H^\circ$  indicate the non-spontaneity and the endothermic nature of the hydrolysis process, respectively.

The large activation energies obtained in the present work may support the fact that the reaction takes place between ions of the same charges. Therefore, the electrostatic attraction between the reactants needs much more energy to bring them together in order to form the activated complex, which defined by eqn (4).

In redox reactions involving  $[\text{IrCl}_6]^{2-}$  as a one-equiv. oxidant, a variety of oxidation mechanisms may be suggested. Some of these reactions proceed through the formation of intermediate complexes *via* intervention of free-radicals of either inner-sphere,<sup>1,5,6</sup> or outer-sphere;<sup>9</sup> or by non-radical outer-sphere mechanisms.<sup>8,15–17</sup> On the other hand, some reactions may involve the formation of either binuclear complexes,<sup>10–12</sup> ion-pairs<sup>14</sup> or both inner- and outer-sphere mechanisms.<sup>13</sup>

Although the rate-law expression here provides no information on the nature of electron-transfer, whether it is of inner- or outer-sphere nature, some information may be expected by examining the magnitude of the rate constants and the activation parameters.<sup>31–38</sup> If the rate constant of the redox step is greater than that of the rate of substitution, *i.e.*, the transfer of electrons is faster than the rate of proton release, the reaction is of the outer-sphere type. On the other hand, if the release of protons occurs prior to the electron-transfer process, the reaction should be of an inner sphere nature. Unfortunately, no data is available on either the rate of substitution of tellurium(IV) or the formation constant ( $K_1$ ) at different temperatures, which is required in order to evaluate the rate constants of the principal elementary reaction. Since the  $\text{Te}^{4+}(\text{H}_2\text{O})_6$  is known to be labile,<sup>23–27</sup> whereas  $[\text{IrCl}_6]^{2-}$  is extremely inert for substitution,<sup>14</sup> the rate constant observed in the present redox reaction may be interpreted in terms of either inner- or outer-sphere mechanisms. However, the perturbation in the spectrum of  $[\text{IrCl}_6]^{2-}$  during the progress of reaction (Fig. 1), especially at higher energy, seems larger than would be expected for an outer-sphere mechanism. Again, it has been reported previously<sup>10–12,31–35</sup> that the entropy of activation tends to be more positive for outer-sphere mechanisms, whereas the values of  $\Delta S^\ddagger$  are more negative for inner-sphere mechanisms.<sup>15,16,31–38</sup> As is shown in Table 3, it was found that the entropy of activation

**Table 3** Activation parameters for the apparent rate constants ( $k'$  and  $k''$ ) in the oxidation of tellurium(IV) by iridium(IV) in aqueous perchlorate solutions.  $[\text{Te}^{IV}] = 5 \times 10^{-3}$ ,  $[\text{IrCl}_6]^{2-} = 1.2 \times 10^{-4}$ ,  $[\text{H}^+] = 0.5 \times 10^{-4}$  and  $I = 0.1 \text{ mol dm}^{-3}$

Constant	Parameter				
	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{298}^\ddagger$ kJ mol <sup>-1</sup>	$E_a^\ddagger$ kJ mol <sup>-1</sup>	$A$ mol <sup>-1</sup> s <sup>-1</sup>
$k'$	69.31	−62.21	88.74	72.62	$9.18 \times 10^{10}$
$k''$	29.21	−146.12	72.57	31.31	$3.34 \times 10^5$

**Table 4** The activation parameters of the second-order rate constant in the oxidation of some inorganic compounds of two-equivalent nature by iridium(IV) in aqueous perchlorate solutions

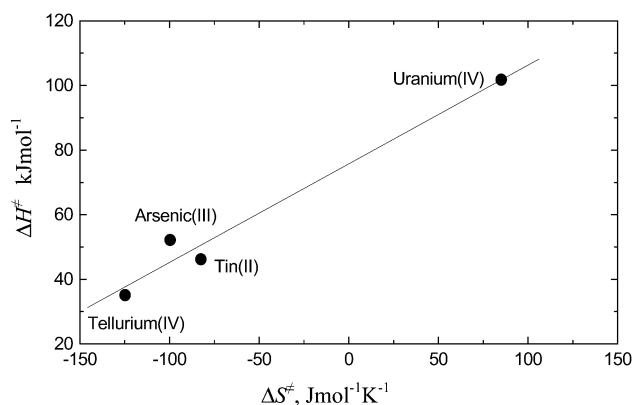
Reductant	Parameter			Reference
	$\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>	
Tellurium(IV)	−124.79	35.08	73.08	This work
Uranium(IV)	+85.03	101.76	76.04	10
Tin(II)	−82.52	46.19	70.87	11
Arsenic(III)	−99.66	52.17	81.86	12

of the present reaction lies in the range of redox reactions of an inner-sphere nature.

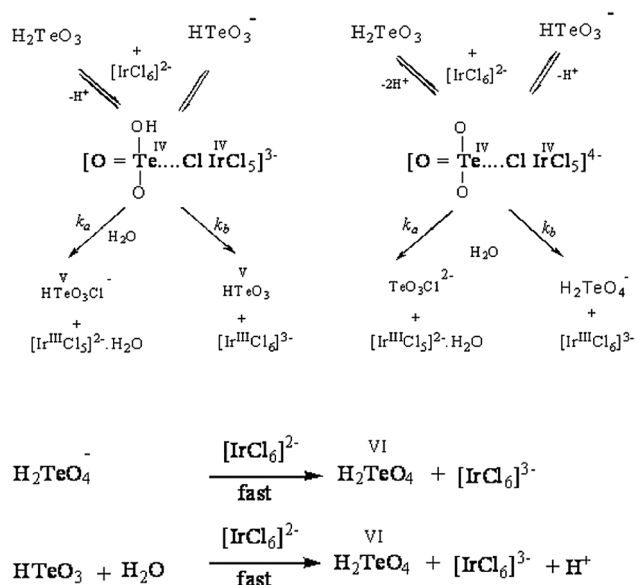
By the above arguments, an outer-sphere mechanism is excluded and, hence, an inner-sphere type mechanism that involves the formation of an intermediate complex, in which one chloride ion from the inert  $[\text{IrCl}_6]^{2-}$  acts as a bridging ligand between the reactants, is the more favorable reaction-path.<sup>39–42</sup> Formation of such a bridge will facilitate the transfer of electrons from tellurium(IV) to iridium(IV) in the rate-determining step.

Again, Leffler and Grunwald<sup>43</sup> have pointed out that many redox reactions show an isokinetic relationship, given by  $\Delta H^\ddagger = \alpha + \beta \Delta S^\ddagger$ . Therefore, the kinetic parameters of the second-order rate constants for the oxidation of some 2-equiv. reductants by hexachloroiridate(IV) are summarized in Table 4. As shown in Fig. 6, a plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  was fairly linear, with  $\alpha = 76 \text{ kJ mol}^{-1}$  and  $\beta = 305 \text{ K}$ . This linearity may indicate that these redox systems follow a similar reaction mechanism. Also, the  $\beta$  value obtained is significant.

In view of the above aspects and the experimental observations, a tentative reaction mechanism consistent with the kinetic results may be suggested, as illustrated in Scheme 1. It involves a fast formation of an intermediate complex prior to the rate-determining step, followed by slow decomposition of such an intermediate through two reaction-paths ( $k_a$ ) and ( $k_b$ ), respectively. Our experimental observations indicate that the final species of the reduced iridium(IV) was  $[\text{IrCl}_6]^{3-}$  and not  $[\text{IrCl}_5]^{2-} \cdot \text{H}_2\text{O}$ . Hence, it seems quite likely that  $k_b$  is the more probable



**Fig. 6** The isokinetic relationship in the oxidation of some inorganic compounds of two-equivalent nature by hexachloroiridate(IV) in aqueous perchlorate solutions.



**Scheme 1** A suggested mechanism for oxidation of tellurium(IV) by hexachloroiridate(V) in aqueous perchlorate solutions.

reaction-path for the decomposition of the formed intermediate to give rise to the reaction products.

## Conclusion

The oxidation of tellurium(IV) as a two-equivalent reductant by iridium(IV) seems to merit an investigation with the aim of shedding more light on the mechanism of the oxidation in terms of the electron-transfer nature. The present oxidation was thought to be a useful test of the postulate, that a metal-ligand transfer occurs if the oxidant is inert, which provides a bridging ligand, and if the reducing agent is substitution labile or it expands its coordination sphere upon oxidation. In addition, this study aimed to kinetically determine the hydrolysis constant of tellurium(IV).

## References

- 1 P. D. Pol, C. P. Kathari and S. T. Nandibewoor, *Transition Met. Chem.*, 2003, **28**, 209–216.
- 2 L. S. A. Diskhtulu, V. H. Rao and S. N. Dindi, *Indian J. Chem., Sect. A: Inorg., Phys., Theor. Anal.*, 1980, **19**, 203–210.
- 3 L. S. A. Dikshitulu, V. H. Reo and P. Vani, *React. Kinet. Catal. Lett.*, 1981, **17**, 103–105.
- 4 L. S. A. Dikshitulu, B. Rambaba and N. Srideri, *Transition Met. Chem.*, 1988, **13**, 39–41.
- 5 K. K. Sen Gupta and U. Chatterjee, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2491–2497; K. K. Sen Gupta, U. Chatterjee and P. K. Sen, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1978, **16**, 767–770; K. K. Sen Gupta, U. Chatterjee and P. K. Sen, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1177–1179; K. K. Sen Gupta and N. Chattacharjee, *J. Phys. Org. Chem.*, 2000, **13**, 157–161.

- 6 E. Pellizetti, E. Mentesi and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1115–1118; H. N. Po, C. F. Lo, N. Jons and R. W. Lee, *Inorg. Chim. Acta*, 1980, **46**, 185–189.
- 7 G. A. Ahmed and R. M. Hassan, *Bull. Pol. Acad. Sci.*, 2001, **49**, 235–244; M. A. El-Korshy and R. M. Hassan, *Bull. Pol. Acad. Sci.*, 1998, **46**, 147–155.
- 8 A. Ayoko, J. F. Lyan and A. T. Ekubo, *Ind. J. Chem. Soc.*, 1992, **31A**, 975–998; K. K. Sen Gupta, S. Dey, S. Sen Gupta and A. Banerjee, *J. Org. Chem.*, 1984, **49**, 5054–5057; R. D. Scurlock, D. D. Gilbert and J. Dekorte, *Inorg. Chem.*, 1985, **24**, 2393–2397.
- 9 D. C. Morris and T. J. Ritter, *J. Chem. Soc., Dalton Trans.*, 1980, 216–219.
- 10 R. M. Hassan, *J. Chem. Soc., Dalton Trans.*, 1991, 3003–3008.
- 11 R. M. Hassan, *Collect. Czech. Chem. Commun.*, 1992, **57**, 326–331.
- 12 R. M. Hassan, *Collect. Czech. Chem. Commun.*, 1992, **57**, 1451–1458.
- 13 A. G. Sykes and R. N. F. Thornley, *J. Chem. Soc. A*, 1970, 232–238.
- 14 R. N. F. Thornley and A. G. Sykes, *J. Chem. Soc. A*, 1970, 1036–1037.
- 15 J. P. Pirk, *Inorg. Chem.*, 1977, **16**, 1381; D. M. Standbury, W. K. Wilmoth, S. Khalaf, H. N. Po and J. E. Byrd, *Inorg. Chem.*, 1980, **19**, 2715–2719; T. W. Newton, *J. Chem. Educ.*, 1968, **45**, 571–575.
- 16 B. J. Gordon, L. L. Williams and N. Sutin, *J. Am. Chem. Soc.*, 1961, **83**, 2061–2065.
- 17 R. K. Whartan, J. F. Ojo and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1975, 1526–1530; C. O. Adedinsowo and A. Adgite, *Inorg. Chem.*, 1979, **18**, 3517–3521; P. Hurwitz and K. Kustin, *Inorg. Chem.*, 1964, **3**, 823–826.
- 18 S. A. Awad, *Electrochim. Acta*, 1968, **13**, 925–936.
- 19 H. Moriyama, I. Fujiwara and T. Nishi, *J. Phys. Chem.*, 1980, **84**, 1801–1805.
- 20 I. A. Poulson and C. S. Garner, *J. Am. Chem. Soc.*, 1962, **84**, 2032–2037.
- 21 M. R. Martinez, PhD thesis, Los Angeles, USA, 1958.
- 22 R. M. Hassan, H. A. Azab and A. Hassan, *Z. Phys. Chem.*, 1987, **268**, 955–960.
- 23 W. S. Melvin and A. Haim, *Inorg. Chem.*, 1977, **16**, 2016–2020.
- 24 B. Grassmann and A. Haim, *J. Am. Chem. Soc.*, 1970, **92**, 4835–4836.
- 25 L. S. A. Dikshitulu and D. Satyanrayana, *Talanta*, 1975, **22**, 313–314.
- 26 C. F. Beas and R. E. Mesmer Jr., *The Hydrolysis of Cations*, A Wiley. Interscience Publication, New York, 1976, p. 388.
- 27 V. A. Kalantre and S. Gokavi, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 2005, **44**, 2084–2093.
- 28 G. Millazo and V. K. Sharma, *Tables of Standard Electrode Potentials*, John Wiley and Sons, New York, 1975, p. 248.
- 29 J. C. Sullivan, *Inorg. Chem.*, 1969, **8**, 313–317.
- 30 R. M. Hassan, *J. Phys. Chem. A*, 2011, **115**, 13338–13345.
- 31 A. Ekstrom and Y. Farrar, *Inorg. Chem.*, 1972, **11**, 2610–2615.

- 32 T. W. Newton and F. B. Baker, *Inorg. Chem.*, 1962, **1**, 368–372.
- 33 F. M. Moore and K. W. Hicks, *Inorg. Chem.*, 1975, **14**, 413–418; K. W. Hicks, D. L. Toppen and R. G. Linck, *Inorg. Chem.*, 1972, **11**, 310–315.
- 34 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, Mc Graw-Hill, New York, 1981.
- 35 N. Sutin, *Acc. Chem. Res.*, 1968, **1**, 225–231.
- 36 R. M. Hassan, *J. Coord. Chem.*, 1992, **27**, 255–266.
- 37 R. A. Marcus, *J. Chem. Phys.*, 1957, **26**, 867–871.
- 38 R. J. Marcus, B. J. Zwolinski and H. Eyring, *J. Phys. Chem.*, 1954, **58**, 432–436.
- 39 W. S. Melvin and A. Haim, *Inorg. Chem.*, 1977, **16**, 2016–2020.
- 40 B. Grossman and A. Haim, *J. Am. Chem. Soc.*, 1970, **92**, 4835–4840.
- 41 R. M. Hassan, *J. Phys. Chem. A*, 2011, **115**, 13338–13345.
- 42 A. Haim, *Prog. Inorg. Chem.*, 1983, **30**, 257–273.
- 43 L. Leffler and E. Grunwald, *Rates and Equilibria of Organic Reactions*, Wiley, New York, 1963.