Inorganica Chimica Acta, 110 (1985) 51–53

Kinetics of Electron Transfer between Ce(IV) Nitrate and Iron(II) Complexes

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Received February 2, 1985

Abstract

The rate constants for the oxidation of some 1,10-phenanthroline and 2,2′-bipyridine complexes of iron(II) by cerium(IV) in nitrate media are reported. In the acidity range investigated (0.05–2.0 M), the predominant reactive species is Ce^{4+}, although $CeOH^{3+}$ also contributes to the reaction progress.

The results are shown to be consistent with the Marcus theory for outer-sphere electron transfer reactions, and the intrinsic parameter for $Ce^{4+/3+}$ couple was estimated.

Introduction

Cerium(IV) is a well-known strong and one-electron oxidant [1]. Despite the variety of tetravalent species of cerium present in solution as a function of the type and concentration of acid used as the reaction medium, investigations of ceric oxidations frequently refer to the oxidant as ‘Ce(IV)’ without specifying the forms involved in the reaction mechanism [2].

The direct experimental determination of the intrinsic reorganizational parameters (*i.e.* self exchange rate) of aquo-ions often gave contradictory results and generally reaction paths involving hydrolyzed species were found to predominate [3]. Indirect methods based on the measure of the rate constants of electron transfer reactions between the metal species and a series of related compounds (such as phenanthroline-like ligand complexes of metal ions, substituted phenothiazines) can allow the estimation of the intrinsic parameter for different redox couples [4, 5].

This paper deals with the investigation of the oxidation of a series of iron(II) complexes by Ce(IV) in nitrate media.

Experimental

Reagents

The iron complexes with 1,10-phenanthroline- and 2,2′-bipyridine-like ligands, referred to as FeL_3^{2+} and listed in Table II, were prepared as described in the literature [6, 7]. The following abbreviations have been used: bipy, 2,2′-bipyridine; dmbipy, 4,4′-dimethyl-2-2′-bipyridine; Clphen, 5-chloro-1,10-phenanthroline; NO_2phen, 5-nitro-1,10-phenanthroline; EE, 4,4′-bis(ethoxycarbonyl)2,2′-bipyridine.

Ce(IV) stock solutions were prepared by anodic oxidation of Ce(III) in nitrate media. The Ce(IV) content was determined by standard oxidimetric titration.

Other chemicals were reagent grade products. Doubly distilled water was used.

TABLE I. Dependence of the Rate Constants for $Fe(EE)_3^{2+}$/Ce(IV) Reaction on Nitric Acid Concentration and Ionic Strength, at 25 °C.

$[HNO_3]$ (M)	k (M^{-1} s^{-1})
0.05	3.8×10^4 [a]
	1.4×10^3 [b]
	3.1×10^2 [c]
0.20	2.0×10^5 [a]
0.50	5.6×10^5 [a]
1.00	9.0×10^5 [a]
2.00	1.7×10^6 [a]

[a] $\mu = 2.0$ M; [b] $\mu = 0.20$ M; [c] $\mu = 0.05$ M.

TABLE II. Redox Potentials of Various Iron Complexes and their Rate Constants with Ce(IV).

N	Compound	$E°$ [a] (Volt *vs.* Ag/0.01 M Ag^+)	k[c] (M^{-1} s^{-1})
I	$(dmbipy)_3Fe(ClO_4)_2$	+0.59[b]	3.2×10^4
II	$(bipy)_3Fe(ClO_4)_2$	+0.75[b]	6.0×10^3
III	$(Clphen)_3Fe(ClO_4)_2$	+0.86[b]	2.1×10^3
IV	$(NO_2phen)_3Fe(ClO_4)_2$	+0.95[b]	5.1×10^2
V	$(EE)_3Fe(ClO_4)_2$	+1.03	3.1×10^2

[a] Measured in 0.1 M TBAP/acetonitrile solution *vs.* a Ag/Ag^+ reference electrode [7]. [b] In agreement with Rollnick and Kochi [8]. [c] Rate constants measured at $\mu = [HNO_3] = 0.05$ M.

0020-1693/85/$3.30

Kinetic Measurements

Kinetic runs were carried out by means of a Durrum stopped-flow spectrophotometer, at 25 °C at the maximum wavelength of the FeL_3^{2+} complexes [6, 7]. The initial concentration of FeL_3^{2+} was 1×10^{-5} M, while the Ce(IV) concentration was ranged between 5×10^{-4} and 5×10^{-3} M. Solutions of both reactants were prepared immediately before use (in the case of Ce(IV) this avoids the formation of polymeric species [9]. The acidity range was from 0.05 to 2.0 M HNO_3.

Measurements were performed at ionic strength $\mu = 0.05, 0.20$ and 2.00 M ($NaNO_3$).

Results

The plots ($A_\infty - A_t$) *vs.* time were found to be linear up to three half lives; the observed pseudo first order rate constants were also linearly dependent on Ce(IV) concentration, suggesting for reaction (1) a second order rate law:

$$FeL_3^{2+} + Ce(IV) \longrightarrow FeL_3^{3+} + Ce(III) \qquad (1)$$

The second order rate constant is strongly dependent on the acidity, as shown by the data listed in Table I for compound V.

Table II reports the second order rate constants for a series of FeL_3^{2+} complexes at a fixed acidity and ionic strength, together with the reduction potentials of $FeL_3^{3+/2+}$ couples [10].

Discussion

It is well known that the aquo-cerium(IV) ion in aqueous solution exists in different hydrolyzed species [11]:

$$Ce^{4+} + H_2O \overset{K_{h1}}{\rightleftharpoons} CeOH^{3+} + H^+ \qquad (2)$$

$$CeOH^{3+} + H_2O \overset{K_{h2}}{\rightleftharpoons} Ce(OH)^{2+} + H^+ \qquad (3)$$

From the data reported for K_{h1} and K_{h2} it is conceivable that at least three different paths can participate in the reaction:

$$Ce^{4+} + FeL_3^{2+} \xrightarrow{k_0} Ce(III) + FeL_3^{3+} \qquad (4)$$

$$CeOH^{3+} + FeL_3^{2+} \xrightarrow{k_1} Ce(III) + FeL_3^{3+} \qquad (5)$$

$$Ce(OH)_2^{2+} + FeL_3^{2+} \xrightarrow{k_2} Ce(III) + FeL_3^{3+} \qquad (6)$$

hence:

$$k_{exp} = \frac{(k_0[H^+]/K_{h1}) + k_1 + (k_2K_{h2}/[H^+])}{([H^+]/K_{h1}) + 1 + (K_{h2}/[H^+])} \qquad (7)$$

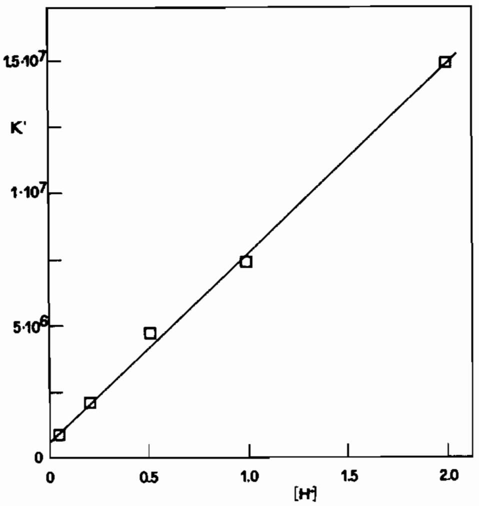

Fig. 1. Plot according to eqn. (7) of $k_{exp}([H^+]^2 + K_{h1}[H^+] + K_{h1}K_{h2})/[H^+]$ (indicated as K') as a function of $[H^+]$ for the reaction of Ce(IV) with $Fe(EE)_3^{2+}$ at 25 °C, $\mu = 2.0$ M.

Figure 1 shows a plot of $(k_{exp}/[H^+])([H^+]^2 + K_{h1}[H^+] + K_{h1}K_{h2})$ as a function of $[H^+]$ for $Fe(EE)_3^{2+}$ using $K_{h1} = 6.4$ M^{-1} and $K_{h2} = 0.12$ M^{-1} [2, 11]. The good linearity suggests that the contribution of the path (6), involving $Ce(OH)_2^{2+}$, is negligible and that the predominant reactive species is Ce^{4+}.

The values of $k_0 = 7.3 \times 10^6$ M^{-1} s^{-1} and $k_1 = 1 \times 10^5$ M^{-1} s^{-1} can be estimated.

Also the effect of ionic strength, although far from the Debye-Hückel region, suggests that the reactions are occurring between highly charged species. In previous investigations on Ce(IV) oxidations in perchlorate or nitrate media the hydrolyzed species were found to be the more important reactive species [13, 14]. In the outer sphere electron transfer however it has been reported that the less hydrolyzed species are the most reactive, although present in lower concentration, such as for example in the case of Co(III) [1, 15] and Mn(III) [4].

In order to verify the dependence of the free energy of activation on the free energy of reaction, as expected for the outer-sphere electron transfer according to the Marcus theory [16], the reaction rates of a series of FeL_3^{2+} complexes with Ce(IV) were measured. Figure 2 shows a plot of the logarithm of the experimental electron transfer rate (at fixed experimental conditions) as a function of the reduction potential of the complexes.

The finding that the plot is in agreement with the expectation of the Marcus model allows, through the well known Marcus cross relation (eqn. (8)), an estimate of the intrinsic parameter of the $Ce^{4+/3+}$ couple starting from k_0 value, determined for $Fe(EE)_3^{2+}$.

The cross relation can be expressed as:

$$\Delta G_{12}^{*} = w_{12} + \lambda_{12}(1 + \Delta G^{\circ\prime}/\lambda_{12})^2/4 \qquad (8)$$

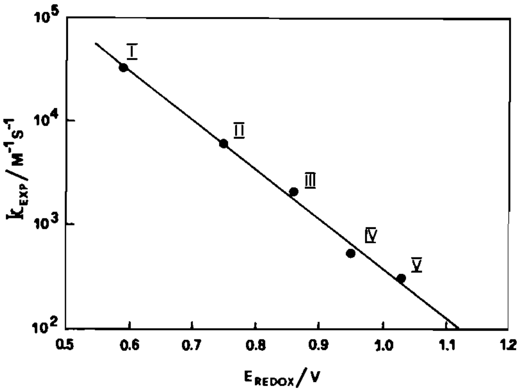

Fig. 2. Plot of the logarithm of the rate constants (at 25 °C and μ = [H^+] = 0.05 M) as a function of the reduction potentials for the reaction between FeL_3^{2+} and Ce(IV). Numbers as in Table II.

where $k = 10^{11} \exp(-\Delta G_{12}^*/RT)$; $\lambda_{12} = 2(\Delta G_{11}^* - w_{11} + \Delta G_{22}^* - w_{22})$ and ΔG_{11}^*, ΔG_{22}^* refer to the self-exchange reactions of the reagents and w_{11} and w_{22} represent the work terms involved in the same reactions; $\Delta G^{\circ} = \Delta G^{\circ} + w_{21} - w_{12}$, where ΔG° is the free energy change of the reaction and w_{21}, w_{12} the work terms required to bring the products or the reactants together at the separation distance in the activated complex. At the ionic strength used the work terms can be tentatively neglected. ΔG° was calculated from the reduction potentials of Ce(IV)/(III) (1.61 V [17]) and $Fe(EE)_3^{3+/2+}$ (1.30–1.35 V extrapolated in the present conditions).

With the reported assumptions and from the experimental data it can be deduced that $\lambda_{12} \cong 35$ kcal mol^{-1}. Since a value of 3×10^8 M^{-1} s^{-1} has been reported for the $Fe(phen)_3^{3+/2+}$ self-exchange rate [18], taking into account the estimation of the work term involved, it can be suggested that ΔG^{**} ($\Delta G^{**} = \Delta G^* - w$) for the $Ce^{4+/3+}$ couple lies in the range 15–16, kcal mol^{-1}. This value compares well with an old estimate of Hush [19, 20] that was difficult to check with the experimental results, since in Ce(IV)/Ce(III) exchange in perchlorate or nitrate media [21] the paths involving hydrolyzed or dimer species largely predominate.

References

1 A. McAuley, *Coord. Chem. Rev.*, *5,* 245 (1970).
2 S. B. Hanna, R. R. Kessler, A. Merbach and S. Ruzicka, *J. Chem. Educ.*, *53,* 524 (1976).
3 W. L. Reynolds and R. W. Lumry, 'Mechanisms of Electron Transfer', Ronald Press, New York, 1966.
4 E. Pelizzetti, *J. Chem. Soc., Dalton Trans.*, 484 (1980); E. Pelizzetti, E. Mentasti and E. Pramauro, *Inorg. Chem.*, *17,* 1688 (1978).
5 A. McAuley, P. R. Norman and O. Olubuyide, *J. Chem. Soc., Dalton Trans.*, 1501 (1984).
6 M. H. Ford-Smith and N. Sutin, *J. Am. Chem. Soc.*, *83,* 1830 (1961).
7 M. Vincenti, E. Pramauro, E. Pelizzetti and T. Geiger, *Atti Accad. Sci. Torino,* in press.
8 K. L. Rollnick and J. K. Kochi, *J. Am. Chem. Soc.*, *104,* 1319 (1982).
9 A. Samuni and G. Czapski, *J. Chem. Soc., Dalton Trans.*, 487 (1973).
10 A. A. Schilt, 'Analytical Applications of 1,10-Phenanthroline and Related Compounds', Pergamon, Oxford, 1969.
11 J. Burgess, 'Metal Ions in Solution', Ellis Horwood, Chichester, 1978.
12 K. G. Everett and D. A. Skoog, *Anal. Chem.*, *43,* 1541 (1971).
13 M. G. Adamson, F. S. Dainton and P. J. Glentworth, *J. Chem. Soc., Faraday Trans.*, *61,* 689 (1964).
14 J. P. Candlin, K. A. Taylor and D. T. Thompson, 'Reactions of Transition Metal Complexes', Elsevier, Amsterdam, 1968.
15 E. Pelizzetti and R. Giordano, *J. Chem. Soc., Dalton Trans.*, 1516 (1979).
16 R. A. Marcus, *Annu. Rev. Phys. Chem.*, *15,* 155 (1964).
17 G. F. Smith and C. A. Getz, *Ind. End. Chem., Anal. Ed.*, *10,* 191 (1938).
18 I. Ruff and M. Zimonyi, *Electrochim. Acta*, *18,* 515 (1973).
19 N. Sutin, *Annu. Rev. Nucl. Sci.*, *12,* 285 (1962).
20 N. S. Hush, *Trans. Faraday Soc.*, *57,* 557 (1961).
21 J. W. Gyder and R. W. Dodson, *J. Am. Chem. Soc.*, *73,* 2890 (1951);
F. R. Duke and F. R. Parker, *J. Am. Chem. Soc.*, *78,* 1540 (1956).