Inorganica Chimica Acta, 76 (1983) L163–L164

A Kinetic Study of Electron Transfer Reactions between Plutonium(VI) and a Series of N-Alkylphenothiazines

E. PELIZZETTI

Istituto di Chimica Analitica, Università di Torino, Turin, Italy

M. WOODS and J. C. SULLIVAN

Chemistry Division, Argonne National Laboratory, Argonne, Ill., U.S.A.

Received November 2, 1982

Introduction

There has been considerable effort expended on the study of redox reactions of the actinide elements in the last decades [1]. In an attempt to characterize the kinetic parameters of outer-sphere electron transfer reactions of the actinides there have been previous studies of the reactions of Np(VI) with N-alkylphenothiazines [2] and substituted 1,10-phenanthroline and 2,2′-bipyridine complexes of Fe(II) [3]. The results obtained in the latter system are fairly consistent with the predictions of reaction rates based on the Marcus formalism [4] while in the former system the measured rate parameters are *ca.* a factor of 100 greater than the predicted values. A plausible reason for such a discrepancy might be too large a thermodynamic driving force for the reactions. If such is the case, the use of Pu(VI) as the oxidant might be expected to provide data that is in closer accord with theory. In this communication we present the results obtained for the oxidation of a series of N-alkylphenothiazines by Pu(VI).

Experimental

Reagents

The characterization of the N-alkylyphenothiazines (PTZ) has been previously described [2] as has the preparation and standardization of the perchloric acid and the Pu(VI) stock solutions [5]. All solutions were prepared in triply distilled water.

Equipment and Procedures

The computer-interfaced stopped-flow instrumentation, as well as the basic procedures and techniques, has been detailed previously [6]. The kinetic runs were followed at the wavelength of maximum absorbance of the cation radical of the PTZ's (see Table I) [7]. The range of initial concentrations was chosen to ensure pseudo-first order conditions: $[PTZ]_o = 1 \times 10^{-5}$ *M*, $[Pu(VI)]_o = 1\text{–}4 \times 10^{-4}$ *M*.

Results

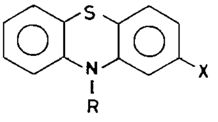
Stoichiometry

The values of the reduction potentials of $PTZ^{\bullet+}$/PTZ (see Table I) and that reported for Pu(VI)/Pu(V), 0.9164 V, [8] along with the excess of Pu(VI) used in these experiments, ensure that the reactions

$$Pu(VI) + PTZ \rightarrow Pu(V) + PTZ^{\bullet+} \qquad (1)$$

go to completion. The verification of the stoichiometry of eqn. 1 was shown in experiments containing an excess of PTZ when the radical concentration was

TABLE I. Characteristics of Investigated Phenothiazines.



Compound	X	R	$E^{o\,a}$	λ, nm^b
I	OH	$CH_2CH_2CH_2N(CH_3)_2$	0.62_5	562
II	H	$CH_2CH_2CH_2N(CH_3)_2$	0.71_5	513
III	Cl	$CH_2CH_2CH_2N(CH_3)_2$	0.78	525
IV	H	$CH_2CH(CH_3)N(CH_3)_2$	0.86_5	515

[a] Determined from equilibrium quotients with Fe(III) at 25 °C $[HClO_4] = 1.00$ *M*, $\mu = 1.0$ *M*. [b] Absorption maximum for the corresponding cation radical.

0020-1693/83/0000-0000/$03.00

TABLE II. Experimental and Calculated Rate Constants for the Reaction of Phenothiazines with Pu(VI).

Compound	k_{exp} [a]	k_{calc} [a,b]	k_{calc}/k_{exp}
I	$(6.07 \pm 0.15) \times 10^5$	2.5×10^7	41
II	$(2.71 \pm 0.04) \times 10^5$	6.6×10^6	24
III	$(1.19 \pm 0.02) \times 10^5$	2.2×10^6	18
IV	$(1.77 \pm 0.04) \times 10^4$	4.7×10^5	26

[a] M^{-1} s^{-1}, $[HClO_4] = 1.00\ M$, Temp. = 25.0 °C, $\mu = 1.0\ M$. [b] Calculated as described in the text.

measured and within experimental uncertainty $\Delta[PTZ^{\bullet+}]/\Delta[Pu(VI)] = 1$.

Kinetics

The integrated form of a first-order rate law provided an adequate description of the experimental data. These observations were interpreted in terms of a second order rate law:

$$d[PTZ^{\bullet+}]/dt = k[PTZ][Pu(VI)] \quad (2)$$

Second order rate constants are listed in Table II.

Discussion

As had been noted in the previous investigation of the oxidation of this series of N-alkylphenothiazines with Np(VI), reaction rates with Pu(VI) as the oxidant again decreased with an increase in the reduction potential of $PTZ^{\bullet+}/PTZ$. Since a plot of the experimental free energy of activation, ΔG_{12}^{+}, as a function of the free energy of reaction, ΔG_{12}°, was linear, rate constants were calculated based on Marcus theory. The work terms were neglected, the free energies of activation for $PTZ^{\bullet+}/PTZ$ were taken as 3.3 kcal mol^{-1} [7] and that for Pu(VI)/Pu(V) was assumed to be equal to that for Np(VI)/Np(V), 12.4 kcal mol^{-1} [5, 8]. Calculated rate constants are listed in Table II.

It will be noted that as predicted for the smaller driving force of the Pu(VI), the discrepancies between the experimental and calculated rate constants are much smaller than in the Np(VI) oxidation [2]. It is noteworthy that aquo ion couples, such as Fe(III)/Fe(II) showed discrepancies of 2–3 orders of magnitude between calculated and experimental rate constants [7, 9]. It was previously advanced that the non-adiabaticity of the process could be responsible for these deviations [10]. In this present study the uncertainty concerning the Pu(VI)/Pu(V) self-exchange rate does not allow further conclusions on the detailed reaction mechanisms.

Acknowledgment

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Nuclear Sciences, U.S. Department of Energy.

References

1 T. W. Newton, 'The Kinetics of the Oxidation–Reduction Reactions of Uranium, Neptunium, Plutonium, and Americium in Aqueous Solutions', Publ. No. TID-26506, U.S. Energy Research and Development Administration Technical Information Center; Oak Ridge, TN, 1975.
2 E. Pelizzetti, M. Woods and J. C. Sullivan, *Inorg. Chem.*, *19*, 524 (1980).
3 E. Pelizzetti, M. Woods and J. C. Sullivan, *Inorg. Chem.*, *20*, 3973 (1981).
4 R. A. Marcus, *Am. Rev. Phys. Chem.*, *15*, 155 (1964).
5 J. Cooper, W. D. Reents, M. Woods, R. Sjoblom and J. C. Sullivan, *Inorg. Chem.*, *16*, 1030 (1977).
6 K. O. Watkins, J. C. Sullivan and E. Deutsch, *Inorg. Chem.*, *13*, 1712 (1974).
7 E. Pelizzetti and E. Mentasti, *Inorg. Chem.*, *18*, 583 (1979).
8 D. Cohen, J. C. Sullivan and J. C. Hindman, *J. Am. Chem. Soc.*, *76*, 352 (1952).
9 C. T. Lin, W. Bottcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, *98*, 6536 (1976).
10 H. Taube, *Adv. Chem. Ser.*, *162*, 127 (1977).