EFFECT OF COMPLEXING AGENTS ON THE DISPROPORTIONATION OF URANIUM (V)

By M. M. Mehta, S. C. Saraiya and A. K. Sundaram, F.A.Sc.

(*Analytical Division, Atomic Energy Establishment, Trombay, Bombay*)

Abstract

The effect of lactate, thiocyanate, sulphate, oxalic acid and fluoride on the disproportionation of uranium (V) formed at the dropping mercury electrode has been studied. The rate constants for the disproportionation reaction are calculated and the results are discussed on the basis of the stability of the complexes.

Introduction

Uranyl ion, in moderately acid solutions, gives two polarographic waves (Harris and Kolthoff, 1945) corresponding to the reduction of uranium (VI) to uranium (V) and to uranium (III). Uranium (V) produced at the electrode, disproportionates in strongly acid solutions (Kolthoff and Harris, 1946) to form uranium (VI) and (IV). This paper deals with the effect of lactate, thiocyanate, sulphate, oxalic acid and fluoride on the disproportionation of uranium (V). The rate constants for the reaction are calculated and the results are discussed on the basis of the stability of the complexes.
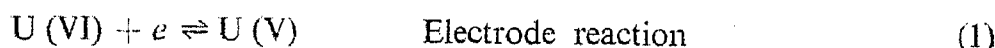
Experimental

The current-potential curves were measured at $30 \pm 0 \cdot 5^{\circ}$ C. using a manual set-up, and a saturated calomel electrode as the reference electrode. All chemicals were of Reagent Grade. The ionic strength was kept at $1 \cdot 0$ by the addition of requisite amounts of sodium perchlorate.

Measurements were made at low acidity ($0 \cdot 01$ M or less) to eliminate the effect of acidity so that the changes in current were due to the effect of complexing agents only. A titration procedure was adopted for obtaining a better accuracy in the measurement of limiting currents. A known volume of the supporting electrolyte containing uranium was taken in the H-cell and the diffusion current after deaeration was measured at $-0 \cdot 6$ V *vs*. S.C.E. The limiting currents were measured after incremental additions of a solution

371

containing the complexing agent. Care was taken to avoid changes in volume by more than 10%. The currents and concentrations were corrected for volume changes.

Results and Discussion

Uranium (V) produced at the electrode due to the reduction of uranium (VI) undergoes disproportionation to form uranium (VI) and (IV) and the reactions can be written as

$$U\ (VI) + e \rightleftharpoons U\ (V) \qquad \text{Electrode reaction} \qquad (1)$$

$$2\ U\ (V) \rightleftharpoons U\ (VI) + U\ (IV) \quad \text{Disproportionation reaction} \qquad (2)$$

Uranium (VI) diffused from the bulk of the solution and that regenerated by the disproportionation reaction reach the electrode and get reduced. The limiting current has therefore a diffusion controlled and a reaction controlled component and the increase in the current beyond that corresponding to a one-electron diffusion controlled reaction is a function of the rate of disproportionation. The rate constant can therefore be calculated by measuring the limiting current of the first wave.

The rate constant is calculated by the method of Koutecky and Koryta (1954) using the following equations:

$$\frac{i_l}{i_d} = 1 + \sum_{i=1}^{\infty} C_i \xi^i \qquad (3)$$

where i_l is the limiting current, i_d is the diffusion current and ξ is defined by

$$\xi = 2akt \qquad (4)$$

where a is the initial concentration of the uranyl ion, t is the drop time and k is the rate constant of the disproportionation reaction. The current for the first wave in a supporting electrolyte containing 0·01 M acid is diffusion-controlled (Kern and Orlemann, 1949). The rate constants calculated by this method for i_l/i_d values up to 1·18 agreed well (Imai, 1957) with those obtained by direct measurements in homogeneous solutions and hence measurements were made in this range only. Values of ξ for experimental values of i_l/i_d were obtained from the data available (loc. cit.) and the rate constant was then calculated from equation (4), a and t being known.

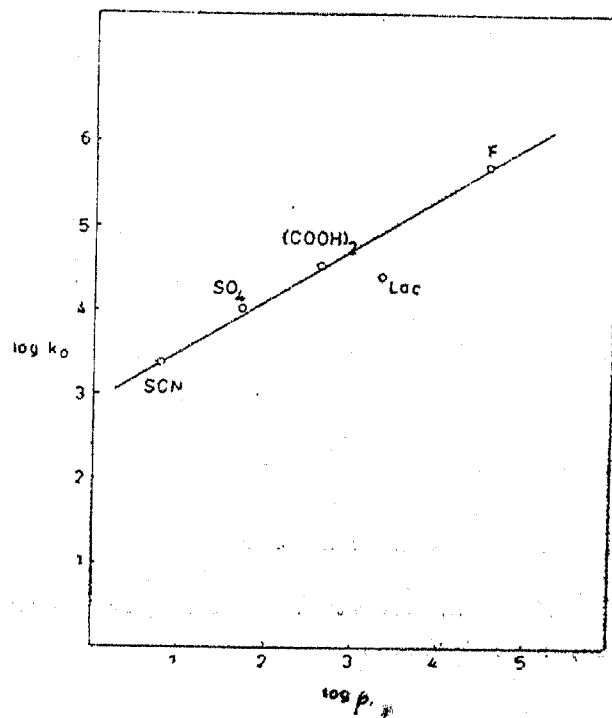The rate constants obtained in the presence of different complexing agents are given in Fig. 1 as a function of concentration. The rate was in
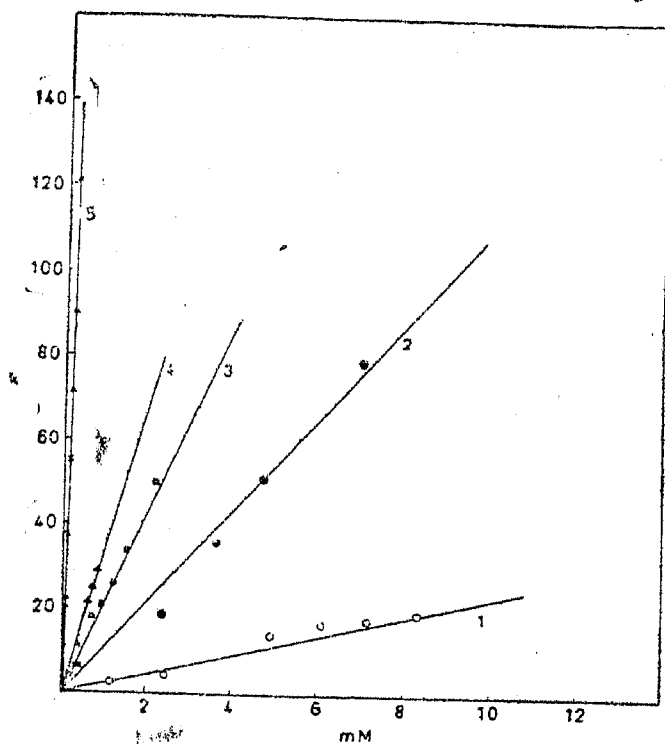
1 THIOCYANATE   4 OXALIC ACID
2 SULPHATE   5 FLUORIDE
3 LACTATE

PLOT OF k vs CONCENTRATION

FIG. 1

PLOT OF log β_1 vs log k_0

FIG. 2

the order: Fluoride > oxalic acid > lactate > sulphate > thiocyanate. The rate (k_0) was calculated at a unit concentration of the complexing agent with a view to compare the effect of various complexing agents from the free ligand concentration calculated from known pK values (Cannan and Kibrik, 1938; McEwen and De Vries, 1957). As the concentration of the complexing agent is increased, uranium (VI) complexes are formed which shift the equilibrium of equation (2) to the right resulting in an increase in the rate of disproportionation. Equilibrium of equation (2) will also be affected by the comparative stability of the uranyl complexes. It is assumed here that the first species is predominant in the solution in view of the large concentrations of uranium and comparatively low concentrations of the ligand in solution. The stability constants of the uranium complexes along with the values of k_0 are listed in Table I. k_0 increases with the increasing stability and a plot of log k_0 vs. log β_1, gives a straight line (Fig. 2). This is in accordance with the observations made by Imai on the effect of nitrate, bromide and chloride. No attempt has been made here to compare the data because of the different experimental conditions of acidity, temperature and ionic strength.

TABLE I

Values of log β_1 and log k_0

Ligand		log β_1	k_0 mole^{-2} sec.$^{-1}$	log k_0
Thiocyanate	..	0·76[1]	2·4×10^{3}	3·38
Sulphate	..	1·7[2]	1·1×10^{4}	4·04
Oxalic Acid	..	2·6[11]	3·5×10^{4}	4·54
Lactate	..	3·36[5]	2·3×10^{4}	4·36
Fluoride	..	4·54[3]	4·8×10^{5}	5·68

REFERENCES

1. Ahrland, S.   ... *Acta Chem. Scand.,* 1949, **3**, 1067.

2. ————————   .. *Ibid.,* 1951, **5**, 1151.

3. ———, Larsson, R. and   *Idid.,* 1956, **10**, 705.
Rosengren, K.

4. Cannan, R. K. and Kibrik, A.   *J. Am. Chem. Soc.,* 1938, **60**, 2314.

5. Crutchfield, C. A. Jr., Mcnabb, *J. Inorg. Nuclear Chem.,* 1962, **24**, 291.
W. M. and Hazel, J. F.

6. Harris, W. E. and Kolthoff,   *J. Am. Chem. Soc.,* 1945, **67**, 1484.
I. M.

7. Imai, H.   .. *Bull. Chem. Soc., Japan,* 1957, **30**, 873.

8. Kern, D. M. H. and   *J. Am. Chem. Soc.,* 1949, **71**, 2102.
Orlemann, E. F.

9. Kolthoff, I. M. and Harris,   *Ibid.,* 1946, **68**, 1175.
W. E.

10. Koutecky, J. and Koryta, J.   *Collection Czechoslov. Chem. Communs.,* 1954, **19**, 845.

11. Krishnamoorthy, K. V. and   *Chem. Revs.,* 1961, **61**, 213.
Harris, G. M.

12. McEwen, D. J. and De Vries, *Can. J. Chem.,* 1957, **35**, 1225.
T.