in the form of the complex, $Cu(C_2O_4)_2^{=}$. A mechanism which leads to the rate law of equations (1) and (2) can be obtained by postulating the oxidation of copper in this complex to the tripositive state.

$$Cu^{II}(C_2O_4)_2^{=} + S_2O_8^{=} \longrightarrow Cu^{III}(C_2O_4)_2^{-} + SO_4\div + SO_4^{=} \quad (10)$$

$$Cu^{II}(C_2O_4)_2^{=} + SO_4\div \longrightarrow Cu^{III}(C_2O_4)_2^{-} + SO_4^{=} \quad (11)$$

$$Cu^{III}(C_2O_4)_2^{-} \longrightarrow Cu^{I}(C_2O_4)^{-} + 2CO_2 \quad (12)$$

$$Cu^{I}(C_2O_4)^{-} + C_2O_4^{=} \longrightarrow Cu^{I}(C_2O_4)_2^{\equiv} \quad (13)$$

$$Cu^{I}(C_2O_4)_2^{\equiv} + S_2O_8^{=} \longrightarrow Cu^{III}(C_2O_4)_2^{-} + 2SO_4^{=} \quad (14)$$

$$Cu^{I}(C_2O_4)_2^{\equiv} + SO_4\div \longrightarrow Cu^{II}(C_2O_4)_2^{=} + SO_4^{=} \quad (15)$$

It is postulated that the rate-determining step is reaction (12), and therefore the rate is first-order with respect to the copper catalyst and zero-order with respect to oxalate and peroxydisulfate. This accounts for the second term on the right-hand side of equation (2), but does not account for the first term. Although it would be convenient to ascribe the first term to the residual copper impurity of the solutions, the spectrographic analyses showed that the impurity was too small for this by a factor of five.

One striking effect on the copper catalysis in this region of concentration is inhibition of the uncatalyzed reaction. The curves of Fig. 3 are very straight and show none of the autocatalytic character of the curves of Fig. 2—this despite the fact that the time for 50% reaction is about the same for the uncatalyzed reaction as for the experiment with 1×10^{-7} M $CuSO_4$. Apparently the $SO_4\div$ radicals are removed by reactions (11) and (15) before they can initiate the chain-reaction with reaction (5).

The increase in rate obtained with a large increase in peroxydisulfate concentration can be explained as due to the simultaneous uncatalyzed reaction. This seems especially likely as the curves resemble those for the uncatalyzed reaction.

The slight decrease in rate observed with an increase in oxalate concentration may be due to a competition between the reactions of the catalyzed and uncatalyzed mechanisms. A more exact explanation of this phenomenon is not readily apparent.

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[CONTRIBUTION FROM THE DEPARTMENT OF RADIATION BIOLOGY, SCHOOL OF MEDICINE AND DENTISTRY, UNIVERSITY OF ROCHESTER]

The Uranyl:Citrate System. II. Polarographic Studies of the 1:1 Complex[1]

BY W. F. NEUMAN, J. R. HAVILL AND ISAAC FELDMAN

Polarographic studies in acid solution with an excess of citrate showed that the 1:1 uranyl citrate complex was present as a dimer and was reduced according to the reactions: (a) (U(VI):citrate)$_2$ + mH$^+$ + 2e = 2U(V):citrate; (b) U(V):citrate + nH$^+$ + e = U(IV):citrate. m and n were approximately unity at pH 4.6 but increased with decreasing pH.

Spectrophotometric studies[2] have shown that uranyl and citrate ions combine to form complexes of two combining ratios, represented empirically by UR and U_2R. Both combining ratios are stable over a wide range of pH, at least 3.0 to 6.0, and are only slightly dissociated. UR appeared to be the more stable ratio and is the principal ion species present when citrate is in excess.

A polarographic investigation was undertaken to gain additional information. Though considerable interest has been shown in the polarography of uranium,[3-11] no report has appeared which is primarily concerned with the uranyl:citrate system.

Preliminary investigation demonstrated that only a limited application of the polarograph could be made. In the first place, reproducible polarograms (without maxima) were obtained only with acid solutions. Secondly, in the pH range of reproducibility, the results were complicated by the presence of several reducible ion-forms: U_2R, UR and uncomplexed uranium. The system was analyzed, therefore, only in acid solutions and in all cases with an excess of citrate to insure that UR was the only combining ratio present in significant concentrations.[2]

Experimental

An automatic recording polarograph (Model XX, E. H. Sargent and Co.)[12] was used throughout these studies. A saturated calomel electrode, connected to the electrolysis cell by means of a saturated potassium chloride–agar bridge, served as an anode.

Stock solutions were prepared from Baker C.P. reagents. Fresh solutions of citric acid were prepared every few days to minimize errors caused by bacterial decomposition. A sample of U_3O_8 (99.95%) obtained from the National Bureau of

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(1) This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York.

(2) I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951).

(3) G. Tishkoff, Thesis, University of Rochester (in preparation); *cf.* also in C. Voegtlin and H. C. Hodge, "The Pharmacology and Toxicology of Uranium Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 125–146.

(4) R. Strubl, *Coll. Czech. Chem. Comm.*, **10**, 466 (1938).

(5) W. E. Harris and I. M. Kolthoff, THIS JOURNAL, **67**, 1484 (1945).

(6) W. E. Harris and I. M. Kolthoff, *ibid.*, **68**, 1175 (1946).

(7) W. E. Harris and I. M. Kolthoff, *ibid.*, **69**, 446 (1947).

(8) H. G. Heal, *Nature*, **157**, 225 (1946).

(9) E. S. Kritchevsky and J. C. Hindman, THIS JOURNAL, **71**, 2096 (1949).

(10) D. M. H. Kern and E. F. Orlemann, *ibid.*, **71**, 2102 (1949).

(11) (a) K. A. Kraus, F. Nelson and G. L. Johnson, *ibid.*, **71**, 2510 (1949); (b) K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949).

(12) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **18**, 734 (1946).

Standards was employed as a reference standard after solution in nitric acid.

Preliminary polarograms were obtained at room temperature, but all the polarograms analyzed were taken at 30.0°. Solutions were deoxygenated with purified nitrogen. Potassium chloride (0.1 *M*) served as a supporting electrolyte. For each polarogram of uranium a corresponding "blank" polarogram was obtained in order to determine the residual current given by the reagents. Gelatin was found necessary for the prevention of maxima. All potentials cited are *vs.* S.C.E.

Results

The voltage–current curves given by uranium in a citrate medium were found to be markedly affected by variation in *p*H. A series of polarograms was obtained with solutions of uranium (2×10^{-4} *M*, $UO_2(NO_3)_2$) in 0.1 *M* citrate in which the *p*H, as measured by a Beckman *p*H meter, was varied from 2.0 to 8.0 by small additions of carbonate-free alkali. The curves, corrected for residual current, are presented in Fig. 1.

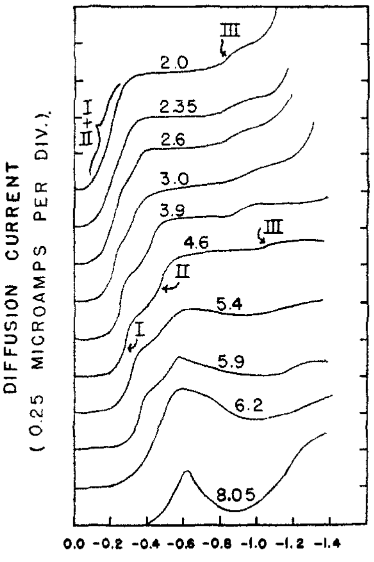

Fig. 1.—Voltage–current curves of 2×10^{-4} *M* $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.1 *M* citrate at various *p*H's. The solutions contained 0.1 *M* KCl and 2.6×10^{-4} % gelatin. The number accompanying each curve indicates the *p*H of the solution studied.

At *p*H 2.0, a single, well-defined wave was observed with an approximate half-wave potential at −0.21 volt together with a very small, ill-defined wave at $E_{1/2} = -0.90$ volt. With *p*H increase, the principal wave, though unchanged in height, developed a point of inflection, becoming two separate waves ($E_{1/2}$'s, −0.30 and −0.45 volt) at *p*H 4.6; the smaller, ill-defined wave nearly disappeared. Above *p*H 5.0, the half-wave potentials continued to become more negative with increasing *p*H, but the appearance of maxima (not suppressed by gelatin) precluded analysis of the results.

Electron Changes.—Gross inspection of the curves in Fig. 1 indicated two principal reduction waves which fused below *p*H 3.

Conventional plots[13] of the data obtained at *p*H's 3.9 and 4.6 for log $i/i_d - i$ *vs.* $E_{d.e.}$ were linear for Wave II only, having an average reciprocal slope of −0.061 ± 0.004 v. This value is in good agreement with theory, −0.060 v., for a one-electron reduction.[13] Wave I gave linear plots of log $i^2/i_d - i$ *vs.* $E_{d.e.}$ which is characteristic of a two-electron reduction of a *dimer*.[13] The average reciprocal slope was −0.027 ± 0.002 v., also in good agreement with theory, −0.030 v., for such a reduction.

Similar results were obtained from *p*H 2.0 to 3.9, despite fusion of the reduction waves, when it was assumed that

$$I_{d.\,\mathrm{Wave\,I}} = I_{d.\,\mathrm{Wave\,II}} = {}^1/_2 I_{d.\,\mathrm{Wave\,I\,and\,II}}$$

Typical data are presented in Fig. 2. Analysis of these data as a single wave resulted either in nonlinear curves or linear plots with reciprocal slopes varying from −0.078 to −0.085.

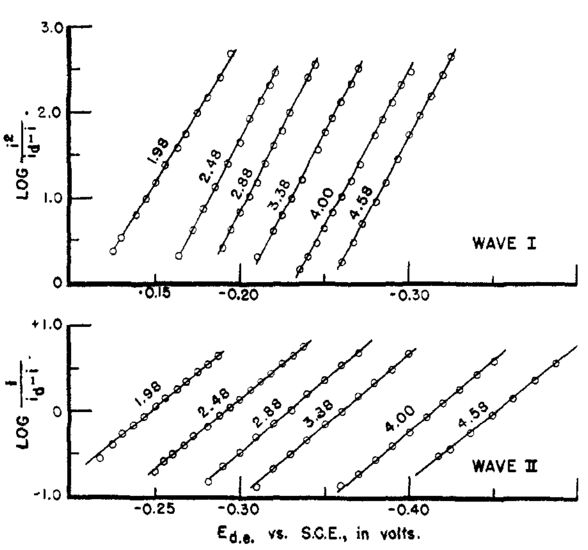

Fig. 2.—Analyses of the electron changes from *p*H 2.0 to 4.6. The solutions contained 5×10^{-4} *M* uranium, 0.1 *M* citrate, 0.1 *M* KCl and 0.004% gelatin. The number accompanying each curve indicates the *p*H of the solution studied.

Solutions of tetravalent uranium, prepared according to Tishkoff,[3] in citrate medium were examined polarographically. No reduction wave of U(IV) was obtained,[14] indicating that the reduction did not proceed beyond the tetravalent state. The electrocapillary curves of the supporting electrolyte and the reducible uranyl system were nearly identical indicating[15] that the reduction waves cannot be attributed to an adsorption process.

The first reduction wave must be assigned to the U(VI):U(V) reduction. The height of the second wave (Fig. 1, *p*H 4.6) is slightly less than that of the first, but by elimination must be assigned to the U(V):U(IV) system. The third wave cannot be assigned with certainty.

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[13] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publ. Inc., New York, N. Y., 1941.

[14] Tetravalent uranium has a tendency to oxidize. On standing, solutions of tetravalent uranium did show the presence of reducible ions. Freshly prepared solutions did not.

[15] E. C. Gregg and W. P. Tyler, THIS JOURNAL, **72**, 4561 (1950).

Effect of Citrate Concentration.—At *p*H 4.6 and 1×10^{-4} *M* $UO_2(NO_3)_2$, the half-wave potentials of both reduction waves were independent of the citrate ion concentration when the U/citrate molar ratio was varied from 1:1 to 1:1000. This verified the fact that at this *p*H no complex ions are formed containing more than one mole of citrate per mole of uranium as shown by previous spectrophotometric studies.[2] It also indicated that there was no change in the number of citrate molecules associated with uranium during its reduction to the tetravalent state.

In Table I are the results obtained at *p*H 2.0, with varying concentrations of citrate. Changes in the $E_{1/2}$'s of Waves I and II noted with concentrations below 0.05 *M* citrate may be attributed to dissociation[2] of the complex as indicated by decreasing I_d. With higher concentrations of citrate, the $E_{1/2}$ of Wave I remained constant. A slight citrate-effect may be indicated by the variability of the $E_{1/2}$ of Wave II.

TABLE I

EFFECT OF CITRATE CONCENTRATION ON POLAROGRAPHIC REDUCTION OF URANYL:CITRATE COMPLEX AT *p*H 2.0

5×10^{-4} *M* $UO_2(NO_3)_2$; 0.1 *M* KCl; 0.004% gelatin

Total citrate concentration, mole/liter	Half-wave potentials *vs.* S.C.E., volts		I_d, μamp.
	Wave I	Wave II	Waves I + II
0.001	0.145	0.209	1.33
.01	.155	.234	2.69
.05	.164	.254	3.33
.10	.168	.249	3.37
.15	.169	.245	3.45
.20	.167	.239	3.50

Effect of *p*H.—The effect of *p*H on the $E_{1/2}$'s of Waves I and II, taken from the logarithmic plots used in wave analysis, is shown graphically in Fig. 3. The observed curves approached linearity at the higher *p*H's with limiting slopes of −0.034 and −0.068 v./*p*H for Waves I and II, respectively.

These limiting slopes are in satisfactory agreement with theory (−0.030 and −0.060) for the reactions

$$(U(VI)\text{:citrate})_2 + H^+ + 2e = 2U(V)\text{:citrate}$$
$$U(V)\text{:citrate} + H^+ + e = U(IV)\text{:citrate}$$

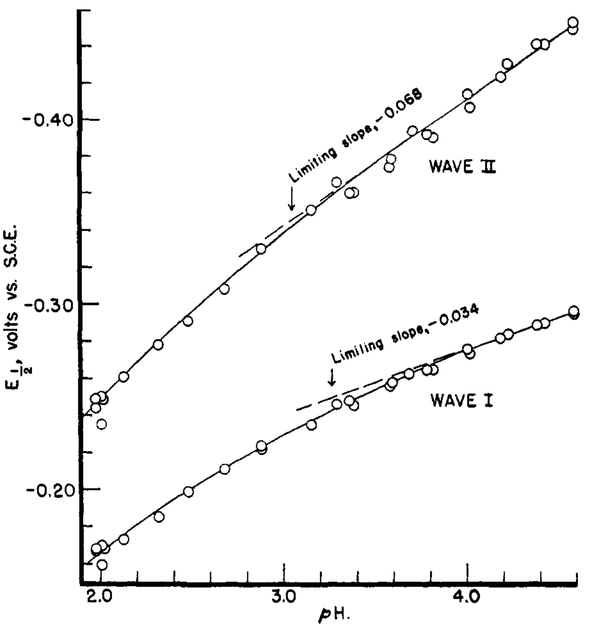

Fig. 3.—An analysis of the effect of *p*H on half-wave potential. The solutions contained 5×10^{-4} *M* uranium, 0.1 *M* citrate, 0.1 *M* KCl and 0.004% gelatin.

The curvature below about *p*H 3.7 indicates that the number of hydrogen ions associated with each reaction increases with decreasing *p*H.

Experiments were performed to show that the changing ionic strength with decreasing *p*H accounted for less than 10% of the total curvature. As previously noted, changes in the concentration of ionized citrate also would not account for the observed results.

Reversibility.—Several of the usual tests of reversibility were performed at *p*H 4.6. The fact that preformed U(IV):citrate did not give an anodic wave indicates that the system, as a whole, was irreversible. In spite of this, both reductions exhibited low temperature coefficients (less than 1.3 mv./deg.), and were analyzed satisfactorily by conventional means.[13]

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