# *Reaction Rate and Electron Transfer Mechanism in Disproportionation Reaction of Uranium (V)**

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In acid solution, sexavalent uranium ($UO_2^{++}$) is reduced to unstable quinquivalent uranium at the dropping mercury electrode, and is regenerated by the disproportionation reaction of the reductant (U(V)) as is schematically shown in the following equations:

$$\mathrm{U(VI)+e=U(V)}: \text{ Electrode Reaction} \quad (1)$$

$$\mathrm{U(V)+U(V)=U(VI)+U(IV)}: \text{ Disproportionation Reaction} \quad (2)$$

Since both the sexavalent uranium diffused from the bulk solution and the one regenerated by the disproportionation reaction reach the electrode and are reduced, the limiting current has a reaction-controlled as well as a diffusion-controlled component[1]. The increase in the current beyond that corresponding to a one-electron diffusion-controlled reduction is a function of the rate of the disproportionation, and one can estimate the rate constant from the measurement of the limiting current.

Hitherto, it has been found that the rate linearly increases with the hydrogen ion concentration[2] and it increases in the presence of chloride[3]. With regard to this effect of chloride it was assumed that the increment in the rate may be assigned to the $\zeta$-potential of the electrode surface.

In this connection, the increase in the rate of some isotopic electron exchange reactions such as Fe(II)—Fe(III)[4], Hg(I)—Hg(II)[5], Ce(III)—Ce(IV)[6], Eu(II)—Eu(III)[7] and Cr(II)—Cr(III)[8] has been observed in homogeneous solutions containing chloride. The present author has also found that the electron transfer of some electrode processes such as the electrolytic reduction of thallous, cadmium and zinc ions under the continuously changing potential is facilitated in solutions containing sulfate, chloride, bromide and iodide in the order given[9]. In this paper a similar effect of various anions on the disproportionation rate process of uranium (V) is investigated, and a tentative reaction mechanism presented.

## Experimental

**Apparatus.**—The current-voltage curves were recorded with a SHIMADZU Model SH-2 photographically recording polarograph, whose maximum current-sensitivity was $2.85\times10^{-9}$ amp./mm./m. The cell used was an H type with triple sintered glass partitions. In two compartments between the test solution and the saturated calomel electrode, the saturated solution of sodium perchlorate and that of sodium chloride were instilled in order to avoid the formation of insoluble potassium perchlorate and also to avoid the contamination of the test solution by chloride. The construction was as follows:

(S.C.E. (Anode))—(Sat. NaCl)—(Sat. $NaClO_4$)—(Test solution-D. M. E. (Cathode)).

The temperature was kept constant within the error of ±0.1°C by a thermostat. With a head of 30 cm. of mercury the mean life-time of the dropping mercury electrode in 2 f sodium perchlorate solution was $5.5_8$ sec. at the applied voltage of $-0.4$ volts vs. S. C. E.

**Reagent.**—All the reagents were of analytical grade. To prepare the stock solution of uranyl perchlorate, uranyl acetate ($UO_2(C_2H_3O_2)_2\cdot 2H_2O$) was evaporated three times with perchloric acid and dissolved in 2 f perchloric acid solution. The test solutions were prepared by diluting this with supporting electrolyte solutions.

The concentration of uranyl ions was determined as follows. Ammonium hydroxide was added to 10 ml. test solution and, after digestion

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* Presented at the Discussion on Polarography held by the Electrochemical Society of Japan in November, 1956, and the 10th Annual Meeting of the Chemical Society of Japan held in April, 1957.

[1] I. M. Kolthoff and W. E. Harris, *J. Am. Chem. Soc.*, **67**, 1484 (1945); **68**, 1175 (1946).

[2] E. F. Orlemann and D. M. Kern, ibid., **75**, 3059 (1953).

[3] J. Koryta and J. Koutecky, *Collection Czechoslov. Chem. Communs.*, **20**, 423 (1955).

[4] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

[5] R, L. Wolfgang and R. W. Dodson, ibid., **56**, 872 (1952).

[6] H. C. Hornig and W. F. Libby, ibid., **56**, 869 (1952).

[7] D. J. Meier and C. S. Garner, ibid., **56**, 853 (1952).

[8] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[9] H. Imai and S. Chaki, This Bulletin, **29**, 498 (1955).

for thirty minutes on a water bath, the precipitate was filtered on a No. 7 Tōyō filter paper. Then, the precipitate was washed with water containing ammonium hydroxide and ignited to red heat. The residue was weighed as $U_3O_8$.

The concentration of perchloric acid in the test solution was determined by titration with the standard solution of sodium hydroxide. Since the basic salt of uranyl perchlorate begins to precipitate at pH greater than 4, methyl orange is qualified for the indicator. The ionic strength was kept at a constant value of 2.1 f by adding sodium perchlorate. In all cases no surface active reagent was used, since it reduced the reaction rate. Nitrogen gas purified by van C. Brunt's method was used to remove the dissolved oxygen in the test solution prior to submission to polarography.

**Current-Voltage Curve.**—The current-voltage curves of uranyl in various supporting electrolytes are shown in Fig. 1. Uranyl developed well-defined polarographic waves in 2 f sodium perchorate solution, there being no polarographic maxima. The half-wave potential of the first wave was $-0.17_0$ volts vs. S. C. E., and that of the second $-0.92_5$ volts vs. S. C. E. The apparent number of electrons transferred per ion was one in the case of the first reduction, and two in the case of the second reduction. When the hydrogen-ion concentration was less than $10^{-3}$ f, the second wave disappeared, while the first wave decreased to a definite height, giving a pure diffusion-controlled current. The first reduction gives quinquevalent uranium, which is unstable in acid solution and disproportionates into sexavalent uranium and quadrivalent uranium. The quinquevalent uranium is reduced to tervalent uranium in the second reduction. It is assumed that in a slightly acidic solution the basic salt of quinquevalent uranium precipitates, and accordingly, the second wave disappears.

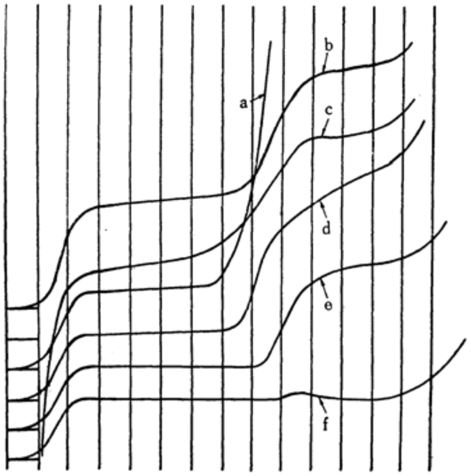

Fig. 1. Current-voltage curves of uranyl in various supporting electrolytes: Each curve starts at 0V vs. S. C. E. and each voltage interval corresponds to 0.1 V. A short horizontal line represents a galvanometer zero line. ($UO_2^{2+}$), 4.22 mf. Temp., 25°C. Ionic strength, 2.1 f.

a ($1\times10^{-1}$ f $H^+$, 2 f $NO_3^-$) b ($1\times10^{-1}$ f $H^+$, 2 f $Cl^-$)

c ($1\times10^{-1}$ f $H^+$, 2 f $Br^-$) d ($1\times10^{-1}$ f′ $H^+$, 2 f $ClO_4^-$)

e ($5\times10^{-3}$ f $H^+$, 2 f $ClO_4^-$) f ($2\times10^{-3}$ f $H^+$, 2 f $ClO_4^-$)

**Estimation of the Rate Constant.**—The disproportionation reaction (equation 2) is of the second order with respect to quinquevalent uranium. Accordingly, the rate of the regeneration of uranium (VI) is given as follows;

$$dU(VI)/dt=1/2\cdot kU(V)^2 \tag{3}$$

where $k$ is the rate constant.

This flux of the sexavalent uranium contributes to the first reduction as well as the flux of the pure diffusion. Hence, one arrives at the equations

$$\partial U(VI)/\partial t=D\partial^2U(VI)/\partial x^2+(2x/3t)\partial U(VI)/\partial x +1/2\cdot kU(V)^2 \tag{4}$$

$$\partial U(V)/\partial t=D\partial^2U(V)/\partial x^2+(2x/3t)\partial U(V)/\partial x -kU(V)^2 \tag{5}$$

the boundary condition being the same as in the case of a pure diffusion, i. e.,

$$\left.\begin{array}{l} t=0,\ x>0;\ U(VI)=a^*,\quad U(V)=0 \\ t>0,\ x=0;\ U(VI)=0,\ \partial U(VI)/\partial x=-\partial U(V)/\partial x \end{array}\right\} \tag{6}$$

where $a^*$ is the concentration of uranyl in the bulk solution, and the diffusion constant ($D$) of the oxidant is assumed to be equal to that of the reductant.

The solution of equations 3 and 4 was given by Orlemann and Kern[2)] by means of the concept of a reaction volume and was followed by Koutecky-Koryta's approximate solution[10)] as is illustrated in the following;

$$\left.\begin{array}{l} \bar{i_l}/\bar{i_d}=1+\sum_{i=1}^{\infty}D_i\xi_1{}^i \\ \xi_1=2a^*kt \end{array}\right\} \tag{7}$$

where $\bar{i_l}$ is the mean limiting current, $\bar{i_d}$ is the mean diffusion-controlled current, $D_i$ is a numerical constant ($D_1=4.716\times10^{-2}$, $D_2=-4.679\times10^{-3}$, $D_3=5.350\times10^{-4}$, $D_4=-6.771\times10^{-5}$, ……) and $t$ is the reaction time.

The pure diffusion-controlled current ($\bar{i_d}$) can be estimated in the solution containing about $10^{-3}$ f hydrogen ion, since in this solution the disproportionation reaction is virtually negligible. In this experiment $\bar{i_l}$ and $\bar{i_d}$ were measured at the applied voltage of $-0.4$ volts vs. S. C. E., where a plateau was given in the current-voltage curve, and $t$ was the mean of the life-time of ten drops of the D. M. E. Thus, the rate constant was calculated and it was confirmed that, as far as the value of $\overline{i_l/i_d}$ did not exceed 1.18, equation 7 gave sufficiently accurate values in comparison

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

TABLE I

EFFECT OF THE HYDROGEN ION ON THE DISPROPORTIONATION RATE CONSTANT

| No. | $(H^+)$ f | $t$ sec. | $E_{1/2}$, $V_{vs.}$ S. C. E. | $\bar{i}_l$ $\mu$A | $\bar{i}_l/\bar{i}_d$ | $\xi$ | $k$ $f^{-1}\cdot sec.^{-1}$ | $k_0$ $f^{-2}\cdot sec.^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.002 | $5.5_8$ | $-0.17_0$ | 14.2 | 1 | 0 | 0 | 0 |
| 2 | 0.005 | $5.5_8$ | $-0.17_0$ | 14.2 | 1 | 0 | 0 | 0 |
| 3 | 0.03 | $5.5_8$ | $-0.17_0$ | 14.5 | $1.02_1$ | 0.48 | 10 | 340 |
| 4 | 0.06 | $5.5_8$ | $-0.17_0$ | 14.9 | $1.04_9$ | 1.16 | 25 | 410 |
| 5 | 0.09 | $5.5_8$ | $-0.17_0$ | 15.3 | $1.07_7$ | 1.93 | 41 | 456 |
| 6 | $0.101_5$ | $5.5_8$ | $-0.17_0$ | 15.4 | $1.08_5$ | 2.19 | 47 | 458 |
| 7 | 0.12 | $5.5_8$ | $-0.17_0$ | 15.5 | $1.09_2$ | 2.40 | 51 | 425 |
| 8 | 0.15 | $5.5_8$ | $-0.17_0$ | 15.7 | $1.10_6$ | 2.86 | 61 | 405 |
| 9 | 0.18 | $5.5_8$ | $-0.17_1$ | 16.0 | $1.12_7$ | 3.62 | 77 | 427 |
| 10 | 0.21 | $5.5_8$ | $-0.17_1$ | 16.3 | $1.14_8$ | 4.43 | 94 | 448 |
| 11 | 0.24 | $5.5_8$ | $-0.17_1$ | 16.5 | $1.16_2$ | 5.08 | 108 | 450 |
| 12 | 0.27 | $5.5_8$ | $-0.17_2$ | 16.8 | $1.18_3$ | — | — | — |
| 13 | 0.30 | $5.5_8$ | $-0.17_2$ | 17.1 | $1.20_4$ | — | — | — |
|  |  |  |  |  |  |  |  | (436)mean |

($a^*=4.22\times10^{-3}$ f, $\mu=2.1$ f ($NaClO_4$))

with those measured in homogeneous solutions[11]. The error for the estimation of the rate constant amounts to ±10%.

## Results and Discussion

**Effect of Hydrogen Ion.**—Uranyl developed no well-defined wave in buffered media, so the acidity of the solution was controlled by perchloric acid. Strictly speaking the hydrogen ion concentration was not equal to the concentration at the electrode surface where the disproportionation reaction occurred. When there was a trace of the dissolved oxygen, the hydrogen ion concentration appreciably decreased at the electrode surface, owing to the formation of the hydroxide ion as the electrolytic reductant. Accordingly, the experiment was carried out after careful removal of the dissolved oxygen.

The hydrogen ion concentration, the limiting current and the rate constant are illustrated in Table I, and the rate constant is plotted against the hydrogen ion concentration in Fig. 2. The experimental conditions are appended to Table I.

From Table I and Fig. 2 one can conclude that the disproportionation reaction of equation 2 is of the first order with respect to the hydrogen ion; the rate constant ($k_0$) reduced to unit hydrogen ion concentration is given by

$$k_0=k/(H^+). \tag{8}$$

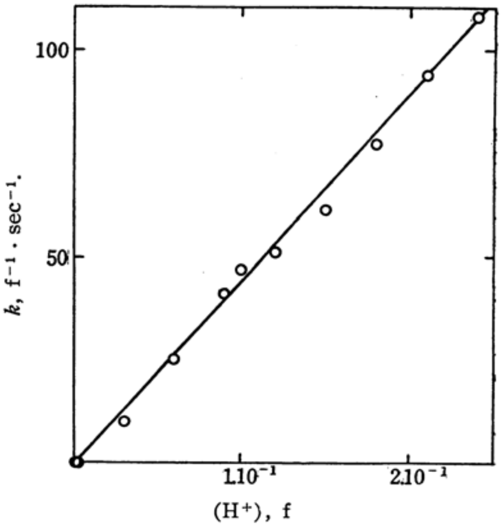

Fig. 2. Effect of the hydrogen ion on the disproportionation rate constant. Supporting electrolyte, 2.1 f $NaClO_4$; Temp., 25°C.

For convenience sake, the comparison of the rate constant will be referred to as $k_0$ in the following description.

**Effect of Chloride.**—The experimental conditions were as follows: the hydrogen ion concentration, $(H^+)=0.04_0$ f; the uranyl concentration, $a^*=1.95_4\times10^{-3}$ f; the reaction time $t=5.5_4$ sec.; the ionic strength, $\mu=2.04$ f; temperature, $T=298.2$°K.

Since the effect of chloride was multiplied by that of the hydrogen ion to yield too great an effect to bear on equation 7, a low concentration of the hydrogen ion was preferable to measure the effect in

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[11] D. M. Kern and E. F. Orlemann, *J. Am. Chem. Soc.*, **71**, 2102 (1949); K. A. Kraus et al., ibid., **71**, 2510 (1949); H. G. Heal and J. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949).

TABLE II

EFFECT OF CHLORIDE ON THE DISPROPORTIONATION RATE CONSTANT

| No. | $(Cl^-)$ f | $t$ sec. | $E_{1/2}$, V vs. S. C. E. | $\overline{i_l}$ $\mu$A | $\overline{i_l}/\overline{i_d}$ | $\xi$ | $k$ $f^{-1}\cdot sec.^{-1}$ | $k_0$ $f^{-2}\cdot sec.^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | $5.5_4$ | $-0.17_0$ | $7.8_2$ | $1.01_9$ | 0.42 | 19 | 475 |
| 2 | 0.2 | $5.5_4$ | $-0.17_2$ | $7.9_4$ | $1.03_5$ | 0.81 | 37 | 925 |
| 3 | 0.4 | $5.5_4$ | $-0.17_4$ | $8.0_1$ | $1.04_3$ | 1.01 | 48 | 1200 |
| 4 | 0.6 | $5.5_4$ | $-0.17_5$ | $8.0_8$ | $1.05_2$ | 1.12 | 52 | 1300 |
| 5 | 0.8 | $5.5_3$ | $-0.17_8$ | $8.1_1$ | $1.05_6$ | 1.34 | 62 | 1550 |
| 6 | 1.0 | $5.5_3$ | $-0.18_0$ | $8.1_3$ | $1.05_9$ | 1.42 | 66 | 1650 |
| 7 | 1.2 | $5.5_3$ | $-0.18_4$ | $8.2_1$ | $1.06_9$ | 1.70 | 79 | 1975 |
| 8 | 1.4 | $5.5_3$ | $-0.18_7$ | $8.2_8$ | $1.07_8$ | 1.96 | 91 | 2275 |
| 9 | 1.6 | $5.5_2$ | $-0.19_1$ | $8.4_4$ | $1.09_9$ | 2.62 | 121 | 3025 |
| 10 | 1.8 | $5.5_1$ | $-0.19_3$ | $8.4_7$ | $1.10_3$ | 2.76 | 128 | 3200 |
| 11 | 2.0 | $5.4_8$ | $-0.19_5$ | $8.5_4$ | $1.11_2$ | 3.08 | 149 | 3725 |

the wide range of the chloride concentration.

Under the above mentioned conditions, the pure diffusion-controlled current was $7.6_8$ microamp., when the hydrogen ion concentration was $5.6\times10^{-3}$ f.

The change in supporting electrolyte may result in the variation in the diffusion constant of a reducible species. Especially, this effect will increase, when a supporting electrolyte acts as a complexing agent. However, in this case the net variation of the diffusion constant is not noticeable; and furthermore, the diffusion-controlled current is proportional to the square root of the diffusion constant. Therefore, the diffusion rate will not play a leading role in the variation of the limiting current, while, it will be a cause of the error in the estimation of the rate constant. On the other hand, the increment of the ζ-potential of the electrode surface in the concentration region above 1 f is less than that in the concentration region below 1 f. Accordingly, the steady increase of the limiting current in the chloride concentration ranging from 0.2 to 2 f is mainly attributable to the increase in the rate constant.

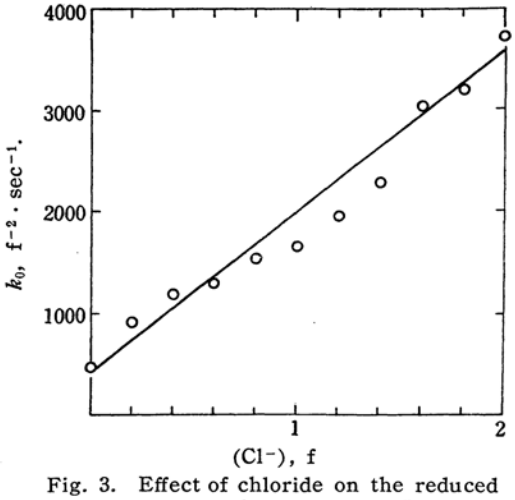

Fig. 3. Effect of chloride on the reduced rate constant, $k_0$. Temp., 25°C; Ionic strength, 2.1 f.

The results of this experiment are illustrated in Table II, and the rate constant is plotted against the chloride concentration in Fig. 3.

From these results it can be seen that the rate of the disproportionation reaction is of the first order with respect to chloride.

The variation of the half-wave potential with the chloride concentration indicates tacitly the existence of the uranyl chloride complex. In this case the kinetic current slightly affects the measurement of the half-wave potential and the mean discrepancy between the 1/4-wave potential and the 3/4-wave potential was about 62 millivolts, which was sufficiently close to the theoretically expected value of a reversible electrode process (59 millivolts)[12]. Hence, assuming that the stability constant of the complex does not vary in the high concentration region of the complexing agent, one can estimate the variation of the coordination number by the equation[13].

$$\bar{p}-\bar{q}=(\mathrm{d}(E_{1/2})_c/\mathrm{d}\log(X^-))\cdot(2.303RT/nF) \qquad (9)$$

where $\bar{p}$ and $\bar{q}$ are the mean coordination number of the higher oxidation state and that of the lower oxidation state, respectively. The plot of the logarithm of the

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[12] T. Thomas, *Collection Czechoslov. Chem. Communs.*, **9**, 12, 81, 150 (1937).

[13] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

chloride concentration against the half-wave potential gives a straight line in the concentration region ranging from 1 f to 2 f as is illustrated in Fig. 4. The value of $\bar{p}-\bar{q}$ calculated from the tangent of the straight line was about unity.

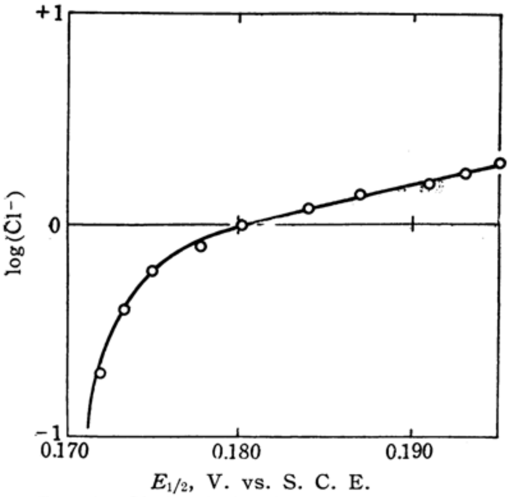

Fig. 4. Shift of the half-wave potential of the first reduction of uranyl by chloride. Temp., 25°C; Ionic strength, 2.1 f.

**Effect of Various Anions.** — By the author's datum the rate constant, $k_0$, was 436 $f^{-2}\cdot sec^{-1}$. in 2 f sodium perchlorate solution. By Koryta and Koutecky[3)] it was 143 $f^{-2}\cdot sec^{-1}$. in 0.4 f sodium perchlorate, and was 700 $f^{-2}\cdot sec^{-1}$. in 3.8 f sodium perchlorate. From these data it can be seen that perchlorate appreciably affects the rate constant, while the effect of perchlorate was smallest in comparison with nitrate and bromide, and in particular, it was negligibly small in comparison with chloride and iodide. Accordingly, sodium perchlorate was qualified for keeping the ionic strength constant.

The experimental conditions were as follows: $(H^+)=0.101_5$ f; $a^*=4.22_5\times10^{-3}$ f; $\mu=2.1$ f; $T=298.2$°K.

The results are illustrated in Table III in which the life-time ($t$) of the D. M. E. appreciably changes with the bromide or the iodide concentration. Since the diffusion-controlled current is proportional to $t^{1/6}$ according to Ilkovic's equation, the variation in the life-time which amounts to 5% does not require any significant calibration for the pure diffusion-controlled current estimated in 2 f sodium perchlorate solution. The value of $\xi$, however, is a linear function of $t$, hence, the variation of the reaction time was taken into account.

In Figs. 5 and 6 is plotted the anion concentration against the limiting current and the rate constant, respectively. In all cases the rate constant is a linear function of the anion concentration. This leads to the following equation;

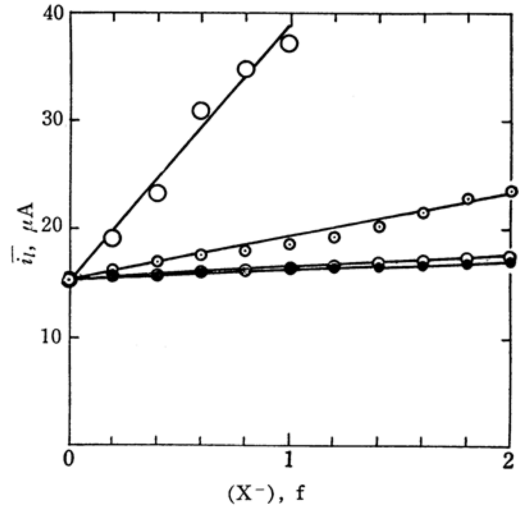

Fig. 5. Variation of the limiting current with the concentration of various anions. Temp., 25°C. Ionic strength, 2.1 f. $(H^+)$, $0.101_5$ f. ●···$NO_3^-$, ○···$Br^-$, ⊙···$Cl^-$, ○···$I^-$.

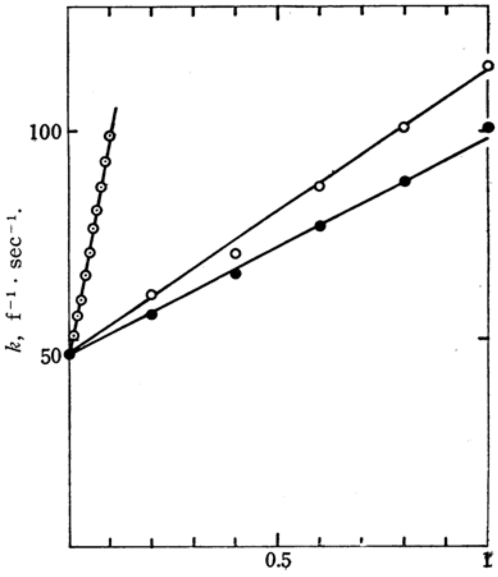

Fig. 6. Effect of various anions on the disproportionation rate constant. Temp., 25°C. Ionic strength, 2.1 f. ●···$NO_3^-$, ○···$Br^-$, ⊙···$Cl^-$.

TABLE III

COMPARISON OF THE EFFECT OF NITRATE, BROMIDE, CHLORIDE AND IODIDE ON THE DISPROPORTIONATION RATE CONSTANT

| | No. | $(X^-)$ f | $t$ sec. | $\overline{i_l}$ $\mu$A | $\overline{i_l}/\overline{i_d}$ | $\xi$ | $k$ $f^{-1}\cdot sec.^{-1}$ | $k_0$ $f^{-2}\cdot sec.^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $NO_3^-$ | 1 | 0 | $5.5_6$ | 15.4 | $1.08_5$ | 2.19 | 47 | 458 |
| | 2 | 0.2 | $5.5_6$ | 15.6 | $1.09_9$ | 2.63 | 56 | 550 |
| | 3 | 0.4 | $5.5_6$ | 15.8 | $1.11_3$ | 3.11 | 66 | 650 |
| | 4 | 0.6 | $5.5_6$ | 16.0 | $1.12_7$ | 3.62 | 77 | 758 |
| | 5 | 0.8 | $5.5_6$ | 16.2 | $1.14_1$ | 4.14 | 88 | 866 |
| | 6 | 1.0 | $5.5_5$ | 16.4 | $1.15_5$ | 4.75 | 101 | 995 |
| | 7 | 1.2 | $5.5_5$ | 16.6 | $1.16_9$ | 5.45 | 116 | 1143 |
| | 8 | 1.4 | $5.5_4$ | 16.8 | $1.18_8$ | 6.18 | 131 | 1291 |
| | 9 | 1.6 | $5.5_4$ | 17.0 | $1.19_7$ | — | — | — |
| $Br^-$ | 1 | 0 | $5.5_8$ | 15.4 | $1.08_5$ | 2.19 | 47 | 458 |
| | 2 | 0.2 | $5.5_4$ | 15.7 | $1.10_6$ | 2.86 | 61 | 598 |
| | 3 | 0.4 | $5.5_0$ | 15.9 | $1.12_0$ | 3.35 | 71 | 700 |
| | 4 | 0.6 | $5.4_5$ | 16.0 | $1.12_7$ | 3.62 | 77 | 758 |
| | 5 | 0.8 | $5.4_1$ | 16.4 | $1.15_5$ | 4.75 | 101 | 995 |
| | 6 | 1.0 | $5.3_9$ | 16.7 | $1.17_6$ | 5.82 | 124 | 1222 |
| | 7 | 1.2 | $5.3_7$ | 16.9 | $1.19_0$ | — | — | — |
| $Cl^-$ | 1 | 0 | $5.6_0$ | 15.6 | $1.09_1$ | 2.37 | 47 | 461 |
| | 2 | 0.04 | $5.6_0$ | 15.8 | $1.10_5$ | 2.83 | 56 | 551 |
| | 3 | 0.08 | $5.6_0$ | 16.0 | $1.11_9$ | 3.32 | 66 | 646 |
| | 4 | 0.12 | $5.6_0$ | 16.3 | $1.13_6$ | 3.96 | 78 | 770 |
| | 5 | 0.16 | $5.6_0$ | 16.4 | $1.14_7$ | 4.38 | 87 | 852 |
| | 6 | 0.20 | $5.6_0$ | 16.6 | $1.16_1$ | 5.04 | 99 | 973 |
| | 7 | 0.40 | $5.5_8$ | 17.4 | $1.22_5$ | — | — | — |
| $I^-$ | 1 | 0 | $5.5_8$ | 15.4 | $1.08_5$ | 2.19 | 47 | 458 |
| | 2 | 0.2 | $4.7_5$ | 19.1 | $1.34_5$ | — | — | — |

TABLE IV

TEMPERATURE DEPENDENCE OF THE LIMITING CURRENT AND THE DISPROPORTIONATION RATE CONSTANT

| | $T°K$ | 281 | 285 | 289 | 293 | 297 | 301 | 305 | 309 |
|---|---|---|---|---|---|---|---|---|---|
| $\overline{i_d}$ | $t$, sec. | $5.8_0$ | $5.7_4$ | $5.6_8$ | $5.6_4$ | $5.6_0$ | $5.5_6$ | $5.5_2$ | $5.4_9$ |
| | $\overline{i_d}$, $\mu$A | 10.6 | 11.4 | 12.1 | 12.9 | 13.7 | 14.4 | 15.2 | 15.9 |
| $(H^+)$ | $t$, sec. | $5.8_0$ | $5.7_4$ | $5.6_8$ | $5.6_4$ | $5.6_0$ | $5.5_6$ | $5.5_2$ | $5.4_9$ |
| | $\overline{i_l}$, $\mu$A. | 10.9 | 11.8 | 12.7 | 13.6 | 14.6 | 15.6 | 16.6 | 17.6 |
| | $\overline{i_l}/\overline{i_d}$ | $1.02_8$ | $1.03_5$ | $1.05_0$ | $1.05_4$ | $1.06_6$ | $1.08_3$ | $1.09_2$ | $1.10_7$ |
| | $\xi$ | 0.65 | 0.82 | 1.19 | 1.29 | 1.61 | 2.12 | 2.40 | 2.90 |
| | $k$, $f^{-1}\cdot sec.^{-1}$ | 13 | 17 | 25 | 27 | 34 | 45 | 52 | 63 |
| $(H^+, Cl^-)$ | $t$, sec. | $5.8_0$ | $5.7_4$ | $5.6_8$ | $5.6_4$ | $5.6_0$ | $5.5_6$ | $5.5_2$ | $5.4_9$ |
| | $\overline{i_l}$, $\mu$A. | 11.0 | 12.0 | 13.0 | 14.1 | 15.2 | 16.5 | 17.9 | 19.3 |
| | $\overline{i_l}/\overline{i_d}$ | $1.03_8$ | $1.05_3$ | $1.07_4$ | $1.09_3$ | $1.10_9$ | $1.14_6$ | $1.17_8$ | $1.21_4$ |
| | $\xi$ | 0.89 | 1.26 | 1.84 | 2.44 | 2.96 | 4.34 | (5.92) | — |
| | $k$, $f^{-1}\cdot sec.^{-1}$ | 19 | 26 | 38 | 51 | 63 | 93 | (127) | — |
| $(H^+, Br^-)$ | $t$, sec. | $5.5_9$ | $5.5_4$ | $5.5_0$ | $5.4_6$ | $5.4_3$ | $5.4_0$ | $5.3_7$ | $5.3_5$ |
| | $\overline{i_l}$, $\mu$A. | 11.1 | 12.1 | 13.2 | 14.4 | 15.7 | 17.1 | 18.6 | 20.3 |
| | $\overline{i_l}/\overline{i_d}$ | $1.04_7$ | $1.06_1$ | $1.09_1$ | $1.11_6$ | $1.14_6$ | $1.18_8$ | $1.22_4$ | $1.27_7$ |
| | $\xi$ | 1.11 | 1.47 | 2.37 | 3.21 | 4.34 | (6.48) | — | — |
| | $k$, $f^{-1}\cdot sec.^{-1}$ | 24 | 31 | 51 | 70 | 95 | (142) | — | — |

$(a^* = 4.22 \times 10^{-3}$ f)

$$\mathrm{d}U(V)/\mathrm{d}t=k_0^0\cdot(\mathrm{X}^-)\cdot U(V)^2 \qquad (10)$$

where $(\mathrm{X}^-)$ is the anion concentration. Thus, it can be concluded that the disproportionation reaction of uranium (V) is of the third order in this case. In view of the fact that the diffusion-controlled current of the cadmium ion increases in the presence of bromide and iodide, the increase in the limiting current of Table III can not be solely assigned to the increase in the disproportionation rate, but it may presumably include the effect of the $\zeta$-potential. In this connection, it is noteworthy that a polarographic maximum appears in the test solution containing 1 f iodide. Furthermore, iodide was oxidized to iodine by perchloric acid in the test solution. Hence, the data in Table III are ill-defined in the cases of bromide and iodide.

The apparent half-wave potential was ill-defined in the solution containing iodide on account of the anodic current flowing at more negative potentials than the reduction potential of uranyl. Also, this effect exists in the case of bromide (cf. Fig. 1). However, it could be confirmed from the measurement in the solution containing low concentration bromide that the half-wave potential was slightly shifted by the presence of bromide. Similarly, the effect of nitrate was too small to deserve any attention**. However, the half-wave potential was appreciably shifted by chloride. It is noteworthy that a parallelism lies between the shift of the half-wave potential and the rate constant, except for the case of the hydrogen ion which does not affect the half-wave potential but increases the rate constant (cf. Table I).

From these results one can conclude that uranyl complex, whose change of the complexity is predominant in the course of the uranyl reduction, is liable to increase the rate of the disproportionation.

**Temperature Dependence of the Rate Constant.** — Test solutions containing $0.101_5$ f hydrogen ion, $0.101_5$ f hydrogen ion and 0.1 f chloride, and $0.101_5$ f hydrogen ion and 1 f bromide were prepared, and each solution was represented by $(\mathrm{H}^+)$, $(\mathrm{H}^+, \mathrm{Cl}^-)$ and $(\mathrm{H}^+, \mathrm{Br}^-)$, respectively, in the following description. The ionic strength of each solution was maintained at 2.1 f. The other experimental conditions are appended to Table IV. The experiment was carried out at the temperature ranging from 280°K to 310°K, and the results are illustrated in Table IV.

The temperature dependence of the pure diffusion-controlled current and of the limiting current is illustrated in Fig. 7. In Fig. 7 the variation of the pure diffusion-controlled current is about 1.9%/deg., which corresponds to the theoretically expected value. On the other hand, the variation in the limiting current is greater than the pure diffusion-controlled current, and it becomes greater in the solution of $(\mathrm{H}^+)$, $(\mathrm{H}^+, \mathrm{Cl}^-)$, $(\mathrm{H}^+, \mathrm{Br}^-)$ in the order given. As was previously described, the variation in the life-time of the D. M. E. did not appreciably affect the pure diffusion-controlled current. The variation of the reaction time, however, was taken into account and the rate constant was calculated.

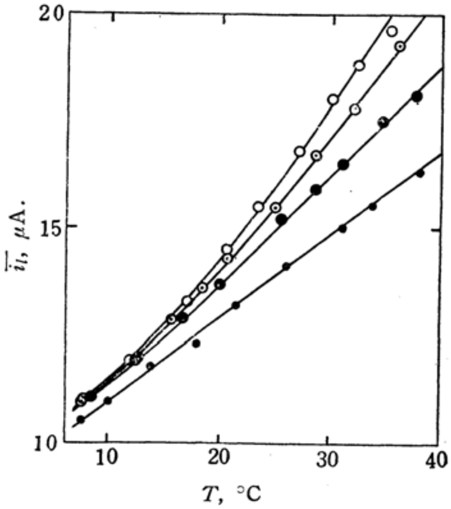

Fig. 7. Temperature dependence of the limiting current. Ionic strength, 2.1 f. $(\mathrm{UO_2}^{2+})$, 4.22 mf. • ···pure diffusion-controlled current, ●···0.1 f $\mathrm{H}^+$, ⊙···0.1 f $\mathrm{H}^+$+0.1 f $\mathrm{Cl}^-$, ○···0.1 f $\mathrm{H}^+$+1 f $\mathrm{Br}^-$.

In Fig. 8 the logarithm of the rate constant is plotted against the reciprocal of the temperature, and the plot gives a good linear relation in every case. From the tangent of the plot the heat of activation $(\Delta H^*)$ was calculated by Arrhenius's

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** In this connection the existence of the uranyl nitrate complex can be observed in the catalytic reduction of nitrate at the reduction potential of quinquevalent uranium. For instance, this phenomenon can be observed in Fig. 1 as a drastic increase of the second wave of uranyl in 2 f sodium nitrate solution. Recently, a detailed investigation of this catalytic current was reported by Koryta[14].

[14] J. Koryta, *Collection Czechoslov. Chem. Communs.*, **20**, 667 (1955).

equation. The heat of activation ($\Delta H^{\ddagger}$) was calculated by equation 11 in order to apply the absolute rate expression.

$$\Delta H^{*}=\Delta H^{\ddagger}+RT \qquad (11)$$

and the entropy of activation ($\Delta S^{\ddagger}$) was calculated from the equation

$$k=(eKT/h)\cdot e^{-\Delta H^{\ddagger}/RT}\cdot e^{\Delta S^{\ddagger}/R} \qquad (12)$$

where $K$ is the Boltzmann constant and the other symbols have their usual significance. The free energy of activation ($\Delta F^{\ddagger}$) was calculated by the equation

$$\Delta F^{\ddagger}=\Delta H^{\ddagger}-T\Delta S^{\ddagger} \qquad (13)$$

All these data are illustrated in Table V.

TABLE V

THE HEAT OF ACTIVATION, $\Delta H^{*,\ddagger}$, THE ENTROPY OF ACTIVATION, $\Delta S^{\ddagger}$, AND THE FREE ENERGY OF ACTIVATION, $\Delta F^{\ddagger}$, OF THE DISPROPORTIONATION REACTION OF U(V)

| Medium | $\Delta H^{*}$ kcal./mole | $\Delta H^{\ddagger}$ kcal./mole | $\Delta S^{\ddagger}$ e. u. | $\Delta F^{\ddagger}$ kcal. |
|---|---|---|---|---|
| 2 f $NaClO_4$ +0.1 f $H^+$ | 10.8 | 10.2 | −17.1 | 15.2 |
| 1.9 f $NaClO_4$ +0.1f $H^+$+0.1f NaCl | 13.3 | 12.7 | −2.7 | 14.1 |
| 1f f $NaClO_4$ +0.1f $H^+$+1f NaBr | 15.4 | 14.8 | +0.4 | 14.7 |

(Ionic strength was kept at 2.1 f with $NaClO_4$.)

It seems from the entropy of activation that the specific function is performed by the hydrogen ion in the actual mechanism involving a different character from those of chloride and bromide.

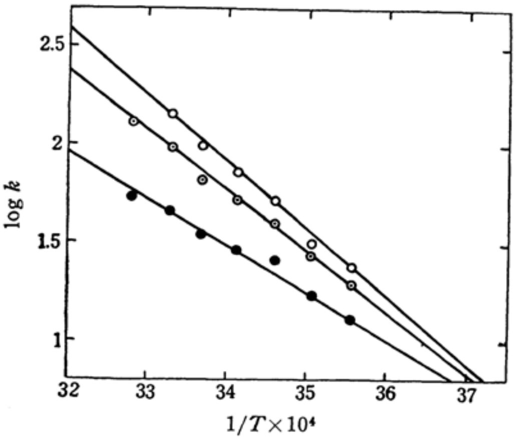

Fig. 8. Temperature dependence of the disproportionation rate constant. Ionic strength, 2.1 f. ●…0.1 f $H^+$, ⊙…0.1 f $H^+$+0.1 f $Cl^-$, ○…0.1 f $H^+$+1 f $Br^-$.

With regard to the function of the hydrogen ion, F. R. Duke and M. C. Pinkerton[15] have proposed a tentative mechanism, that is, the hydrogen ion increases the concentration of $UOOH^{2+}$ (cf. eq. 15) pertaining to the disproportionation and the charge transfer is not performed by the proton transfer but by the hydroxyl-radical transfer. This postulation is supported by the author's result giving a good agreement with an isotopic electron exchange reaction of $Fe^{2+}-FeOH^{2+}$[4], in which the entropy of activation is −18 e. u., the free energy of activation is 12.2 kcal. and the mechanism of the charge transfer is assumed to be a typical case of the bridge transfer of the hydroxyl-radical. Accordingly, the following mechanism can be confirmed:

$$UO_2^{2+}+e=UO_2^{+}\ :$$

Electrode Reaction (14)

$$UO_2^{+}+H^{+}\rightleftarrows UOOH^{2+} \qquad (15)$$

$$UO_2^{+}+UOOH^{2+}=HOUO_2^{+}+OU^{2+}\ :$$

Disproportionation Reaction (16)

Since we may consider $UOOH^{2+}$ to be a strong acid, the equilibrium in equation 15 shifts toward the right-hand side and results in the increase in the concentration of $UOOH^{2+}$ with the increase in the hydrogen ion concentration. This effect will result in the increase in the disproportionation rate in an acid solution.

On the contrary, an alternate mechanism can be proposed to the cases of chloride and bromide. In Table V it can be seen that the most rapid reaction path has a less negative entropy of activation. Furthermore, in the cases of ($H^+$, $Cl^-$) and ($H^+$, $Br^-$) the entropies of activation are virtually equal to zero. Since it has been reasoned that the entropy of activation is approximately zero for a unimolecular reaction, the disproportionation is likely to proceed as a unimolecular reaction in these cases. The rate of the disproportionation is of the first order with respect to the anion concentration, and the existence of the uranyl nitrate- or chloride-complex is confirmed, as is previously described. These results lead to the ease of the formation of uranyl complex involving a sharing of the coordination sphere by two center atoms as is formulated in the following:

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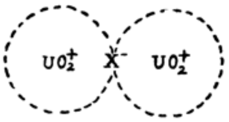
[15] F. R. Duke and M. C. Pinkerton, *J. Am. Chem. Soc.*, **73**, 2361 (1951).



In this state the structure of the two complexes is symmetrical with respect to the shared anion, hence, one can predict that the exchange rate will increase as is clearly enunciated by Libby[16] by applying a quantum mechanical expression of the exchange frequency of the hydrogen molecular ion. It is assumed that the difference in the rate constant among various anions will depend upon the firmness of the coordination, and upon the interatomic distance.

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[16] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).