fact that the labile periodate can be removed from aged acid solutions without affecting either the absorption spectrum or the stability (with respect to reduction by the solvent) shows that the labile periodate is not responsible for stabilization of the cobaltic state. The explanation indicated is that a polynuclear species is formed which contains more cobalt than iodine atoms. Apparently this polymer is slowly built up from simpler species until an appreciable concentration of the species exists which has an empirical formula containing 4 cobalt atoms and 3 periodate groups with a charge of -3. This species in turn has limited solubility in 2 M perchloric acid and so precipitates. The species has an average simple formula weight of 1102 ± 20 as determined from all determinations of the cobalt, iodine and free hydrogen ion.

A plausible species which satisfies the requirements of stoichiometry and which has a formula

weight of 1124 is $H_3[Co_4I_3O_{30}H_{24}]$. One of the several isomeric structures is
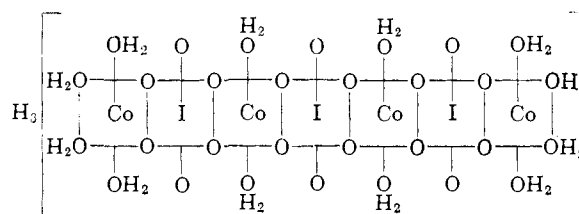
ADDED IN PROOF.—An alternative formulation which is equally probable on the basis of evidence presented here is $H_3[Co_4I_3O_{24}H_{12}] \cdot xH_2O$ with a structure similar to that determined by H. T. Evans (*J. Am. Chem. Soc.*, **70**, 1292 (1948)) for $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$.

An Isotopic Exchange Study of the U(IV)-U(V)-U(VI) Equilibrium in Aqueous Perchlorate Solutions[1]

BY B. J. MASTERS AND LARRY L. SCHWARTZ

Measurements of U(IV)-U*(VI) exchange have been employed in an investigation of the reaction U(IV) + U(VI) $\rightleftharpoons$ 2U(V) under conditions of chemical equilibrium in perchlorate media of ionic strength 2.0. A successful separation of this exchange path from the competitive exchange reaction was found possible at U(IV) concentrations below 0.01 M and temperatures of 25° and higher. The equilibrium reaction was found to obey the rate law $R_{xg} = k[U^{+4}][UO_2^{++}][H^+]^{-3}$, with a rate constant of $k = 2.13 \times 10^{-7} M^2$ sec.$^{-1}$ being observed at 25°. The thermodynamic quantities of activation were found to be $\Delta H^* = 37.5$ kcal./mole and $\Delta S^* = 36$ e.u. The results are consistent with polarographic measurements of the U(IV)-U(V)-U(VI) equilibrium and of the U(V) disproportionation reaction. The U(IV)-U*(VI) exchange rate was found to be strongly accelerated by ultraviolet irradiation.

Introduction

The exchange of uranium isotopes between U-(IV) and U(VI) ions in solution has been the subject of a number of cursory investigations,[2] while more comprehensive kinetic studies have been carried out in hydrochloric acid media by Rona.[3] The system also has been studied in sulfuric acid solutions under the influence of external illumination[4] and in mixed aqueous hydrochloric acid-ethanol media.[5]

The formation of uranium(V) in solutions of uranous and uranyl ions, in accordance with the equilibrium

$$U(IV) + U(VI) \rightleftharpoons 2U(V) \qquad (1)$$
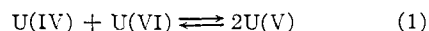
has been demonstrated by Heal[6] and studied

(1) This work was performed under the auspices of the United States Atomic Energy Commission. Presented in part at the 138th A.C.S. Meeting, New York, N. Y., September, 1960.

(2) The following unclassified reports have been issued by the United States Atomic Energy Commission and its contractors: M. B. Allen, RL-4.6.279 (1944); A. Grosse, MDDC-1644 (1948); E. L. King, CB-3605 (1946) and MDDC-813 (1947); E. Rona, AECD-1909 (1948); R. W. Woodward, *et al.*, Y-30 (1947) and Y-184 (1948); D. G. Hill, Y-478 (1949).

(3) E. Rona, *J. Am. Chem. Soc.*, **72**, 4339 (1950), and "Radioisotopes in Scientific Research," edited by R. C. Extermann, Vol. II, Pergamon Press, New York, N. Y., 1958, pp. 296–304.

(4) R. J. Betts, *Can. J. Research*, **26**, 702 (1948).

(5) D. M. Mathews, J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, **63**, 1236 (1959), and A. Indelli and E. S. Amis, *J. Am. Chem. Soc.*, **81**, 4180 (1959).

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

quantitatively by Kraus and Nelson.[7] Assuming the uranium(V) ions formed in (1) to be chemically equivalent, this equilibrium should provide one path for exchange between U(IV) and U(VI), and in the absence of other exchange paths, it should be possible to evaluate the rate constant for the forward step in the equilibrium by means of exchange measurements. The separation and measurement of exchange occurring *via* the path represented by (1) has not previously[2-5] been demonstrated and is the subject of the present investigation.

Experimental

Materials.—Distilled water was redistilled from alkaline permanganate solution before use. Sodium bicarbonate, which was used in small quantities for final adjustment of the pH of some of the exchange solutions, was of analytical reagent grade. Analytical reagent grade 70% perchloric acid was filtered through a fine frit and boiled under reduced pressure in a Pyrex distillation apparatus until all yellow-colored impurities (presumably oxides of chlorine) had been removed. Sodium perchlorate was prepared by neutralizing perchloric acid with a slight excess of analytical reagent grade sodium carbonate. The resulting solution was filtered to remove basic precipitates, then acidified slightly and boiled to expel carbon dioxide, after which solid NaClO₄ was obtained by partial crystallization. A stock solution of NaClO₄ was prepared and analyses were performed by evaporating aliquots, drying at 160° and weighing the anhydrous salt. Uranyl perchlorate stock solution was pre-

(7) K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **73**, 2157 (1951).

pared from spectrochemically analysed uranium oxide which had been depleted with respect to the naturally occurring isotopes U^{234} and U^{235}. After the oxide was dissolved in perchloric acid and diluted with water, the stock U(VI) solution was analysed by reducing with zinc amalgam, oxygenating to insure the conversion of any U(III) present to U(IV) and titrating with standard ceric sulfate solution. Uranous perchlorate stock solution was prepared by electrolysis at a mercury cathode of uranyl perchlorate stock solution until titration with ceric sulfate indicated that reduction to U(IV) was complete. The U(IV) stock solution was tested to insure the absence of chloride ion and stored under argon in an inert atmosphere buret. The radiotracer U^{233} was obtained as the oxide, dissolved in nitric acid and separated from daughter activities by adsorption from a concentrated hydrochloric acid solution on a Dowex 1-X10 anion exchange column. After being eluted with water and fumed down with concentrated $HClO_4$, the radiotracer was added to a portion of the U(VI) stock solution to give a labeled U*(VI) solution containing an isotopic enrichment of about 2% U^{233}.

Run Procedure.—The required amounts of water and stock solutions of $HClO_4$, $NaClO_4$ and labeled U*(VI) were pipetted into a darkened Pyrex reaction flask which was immersed in a constant temperature bath. Argon gas, which had been passed successively through Oxsorbent and a 2 M $NaClO_4$ solution at the temperature of the water bath, was allowed to bubble through the exchange solution in order to provide stirring and to maintain a protective atmosphere over the exchange solution. Unlabeled U(IV) was added to the exchange solution to start the reaction. After equilibration, aliquots of the exchange solution were removed at timed intervals and quenched by transferring to a separatory funnel containing a sufficient amount of 1 M $HClO_4$ to bring the acidity to about 0.5 M. The first such sample removed was designated as the "zero time" sample. A "complete exchange" counting sample was obtained by treating an aliquot of the exchange solution with zinc amalgam and oxygenating briefly in 0.5 M $HClO_4$ in order to convert all of the uranium present to the U(IV) oxidation state.

Separation of the Oxidation States.—Each of the quenched counting samples, including the "complete exchange" sample, was shaken immediately with 5 ml. of a 0.1 M thenoyltrifluoroacetone (TTA) solution in benzene. The benzene layer was washed once with 0.5 M $HClO_4$ solution, and the U(IV) fraction was re-extracted by shaking with 5 ml. of 3 M HCl. This aqueous layer, usually containing about 70% of the U(IV) and virtually none of the U(VI) originally present in the aliquot, was filtered and allowed to stand until radioassay could be performed. The exchange induced by this separation procedure was shown to be insignificant.

Determination of Hydrogen Ion Concentration.—The hydrogen ion concentration of the exchange solution was measured at 23°, using a Beckmann Model G pH meter with a glass electrode and a saturated sodium chloride calomel reference electrode. Calibration curves were obtained from measurements of solutions containing known amounts of perchloric acid made up to an ionic strength of 2.0 with sodium perchlorate, complete dissociation of the acid being assumed.

Uranyl Oxalate Actinometry.—In the ultraviolet irradiation-induced exchange experiment, the light source consisted of a General Electric G4T4/1 germicidal lamp, a four watt low pressure mercury vapor lamp emitting radiation predominantly of wave length 2537 Å. Ten-ml. aliquots of exchange solution were held in reproducible geometry just below the lamp and agitated with bubbling argon during the irradiation. Aliquots of actinometer solution, 0.01 M in uranyl sulfate and 0.05 M in oxalic acid, were irradiated under identical conditions. Assuming a quantum yield of 0.6 for the decomposition of the actinometer solution,[8] the rate of energy absorption by the 10 ml. aliquot was calculated to be 1.0 × 10^17 quanta per second.

Specific Activity Determinations.—Each 3 M HCl counting sample was shaken with zinc amalgam and oxygenated briefly to insure that all uranium present was in the (IV) oxidation state, after which the optical density was measured at 6500 Å. At this wave length, the molar extinction coefficient of U(IV) in 3 M HCl is about 58 M^{-1}cm.$^{-1}$. An aliquot of the solution containing a known amount of uranium (usually

about 100 μg.) then was spotted onto a platinum disc of about 18 cm.^{2} area. The solution was dried under a heat lamp and the disc was flamed at red heat in order to produce an adherent film of U_3O_8. The total alpha activity of the disc was measured under flowing methane in a windowless proportional counter with external amplifier, sufficient counts being taken to reduce the statistical counting error to less than 1%.

Calculation of Exchange Results.—From each set of counting samples, a series of fractional exchange values was calculated by means of the equation[9]

$$F = (S - S_0)/(S_\infty - S_0) \qquad (2)$$

in which F represents the fractional exchange achieved in the time t, S the specific activity (counts per minute per microgram uranium) of the U(IV) fraction in the sample removed at time t, S_0 the U(IV) specific activity of the "zero time" sample and S_∞ the specific activity of the "complete exchange" sample. A plot of $\ln (1 - F)$ versus t was then made and from the slope of the resulting straight line, the exchange rate was obtained by means of the classical equation[10]

$$R_{xg} = - \frac{[U(IV)][U(VI)]}{[U(IV)] + [U(VI)]} \cdot \frac{d}{dt} \ln (1 - F) \qquad (3)$$

The use of the total U(IV) concentration in equation 3 is justified only if the species U^{+4} and UOH^{+3} exchange rapidly with each other in comparison with the rate of the over-all U(IV)–U(VI) exchange reaction. That such is indeed the case was demonstrated by the observed linearity of the exchange plots, together with comparisons of the observed values of S_0 and S_∞ with those calculated from the known specific activities of the U(IV) and U*(VI) stock solutions.

Results

A preliminary study of this system indicated the presence of two parallel exchange paths, one occurring at a rate proportional to the uranous ion concentration and with an apparent activation energy of about 38 kcal. per mole, the other exhibiting a higher order uranous ion concentration dependence and an apparent activation energy of about 28 kcal. per mole. Since the latter exchange path appeared to be completely analogous to the exchange reaction previously reported by Rona[3] for hydrochloric acid media, further attention was confined to the path which predominates under conditions of low uranous ion concentration and at temperatures in excess of room temperature.

Uranous Ion Dependence—Measurements of the exchange rate at 39.4° were made over a twentyfold range of U(IV) concentrations in solutions of constant ionic strength, acidity and U(VI) concentration. The results of these measurements are presented graphically in Fig. 1(a) and indicate a first-order dependence of the exchange rate upon the total U(IV) concentration. Under the conditions employed in these measurements, uranous ion is approximately one-third hydrolyzed[11] according to the equilibrium

$$U^{+4} + H_2O = UOH^{+3} + H^+ \qquad (4)$$
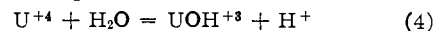
and since less than 0.1% of the total U(IV) is present as hydrolyzed polymers,[12] the exchange reaction may be considered to occur at a rate proportional to the concentration of either of the U(IV) species represented in equation 4. It may be noted that, under the conditions specified in Fig. 1(a), this first-order exchange path predomi-

(9) R. J. Prestwood and A. C. Wahl, ibid., **71**, 3137 (1949).

(10) H. A. C. McKay, Nature, **142**, 997 (1938); R. B. Duffield and M. Calvin, J. Am. Chem. Soc., **68**, 557 (1946).

(11) K. A. Kraus and F. J. Nelson, ibid., **72**, 3901 (1950); ibid., **77**, 3721 (1955).

(12) S. Hietanen, Acta Chem. Scand., **10**, 1531 (1956).

(8) W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc., **52**, 3139 (1930).
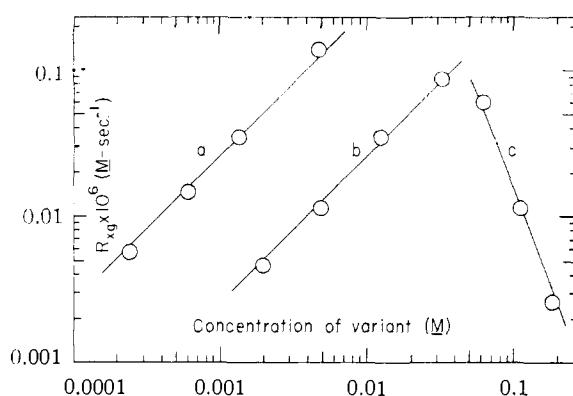
Fig. 1.—Observed exchange rate dependence upon the reactant concentrations at ionic strength 2.0 and 39.4°: (a) [U(IV)] varied at [U(VI)] = 0.0132 M and [H$^+$] = 0.112 M; (b) [U(VI)] varied at [U(IV)] = 0.00132 M and [H$^+$] = 0.112 M; (c) [H$^+$] varied at [U(IV)] = 0.00132 M and [U(VI)] = 0.00484 M. Each experimental point was obtained from a set of seven counting samples. The solid lines represent the theoretical functions $R_{xg}/$[U(IV)] = constant, $R_{xg}/$[U(VI)] = constant and R_{xg}([H$^+$]^3 + 0.0560 [H$^+$]^2) = constant, respectively.

nates up to U(IV) concentrations of about 0.075 M, above which point the higher-order [U(IV)] path predominates.

Uranyl Ion Dependence.—As shown in Fig. 1(b), the exchange reaction exhibits a first-order dependence upon uranyl ion over a seventeen-fold range of UO_2^{++} concentrations, when studied at 39.4° in solutions of constant ionic strength, acidity and U(IV) concentration. The predominant U(VI) species present during these measurements has been assumed to be UO_2^{++}.

Hydrogen Ion Dependence.—In Fig. 1(c) are shown the results of exchange rate measurements over a three-fold range of hydrogen ion concentrations in solutions of constant ionic strength, U(IV) and U(VI) concentrations. It should be noted that, although the total U(IV) concentration was held constant during these measurements, the amount of hydrolysis via reaction 4 varied in accordance with the relation

$$K_H = \frac{(UOH^{+3})(H^+)}{(U^{+4})} \quad (5)$$

the value of the hydrolysis constant K_H being 0.0560 at 39.4° in solutions of ionic strength 2.0.[11] Consequently for a reaction of first-order [U^{+4}] dependence and inverse n^{th} order [H$^+$] dependence, the observed reaction rate at constant U(IV) concentration should be inversely proportional to the quantity [H$^+$]^n + 0.0560[H$^+$]$^{n-1}$. The solid line in Fig. 1(c) represents the calculated function R_{xg}([H$^+$]^3 +0.0560[H$^+$]^2) = constant. The fit of the experimental points to this theoretical curve indicates that the exchange reaction proceeds with an inverse third-order hydrogen ion dependence.

Evaluation of the Rate Constant.—From the observed exchange rate and the rate expression

$$R_{xg} = k\frac{[U^{+4}][UO_2^{++}]}{[H^+]^3} \quad (6)$$

$$= k\frac{[U(IV)][U(VI)]}{[H^+]^3 + K_H [H^+]^2} \quad (7)$$

values of the rate constant k were calculated for all of the measurements at 39.4° and ionic strength 2.0. These calculations yielded a mean value of k = 4.14 × 10^{-6} M^2 sec.$^{-1}$ with a mean deviation of ± 0.38 × 10^{-6} M^2 sec.$^{-1}$.

Temperature Dependence.—Exchange rate measurements were performed at four temperatures and the results are shown in Table I. The tabulated values of K_H were obtained by extrapolating the data of Kraus and Nelson[11] and were used in the calculation of the corresponding exchange rate constants by means of equation 7. The

TABLE I

TEMPERATURE DEPENDENCE OF THE U(IV)–U(VI) EXCHANGE REACTION: [U(IV)] = 0.00122 M, [U(VI)] = 0.00484 M, [H$^+$] = 0.112 M, μ = 2.0

| Temp., °C.	K_H	k × 10^6 (M^2 sec.$^{-1}$)
25.1	0.0238	0.213
32.4	.0370	0.980
39.4	.0560	4.14
47.1	.0870	17.3

linearity of the Arrhenius plot of the data in Table I indicates a satisfactory separation of the exchange path from the path of higher order [U(IV)] dependence and of lower activation energy. The least squares slope of the Arrhenius plot corresponds to an experimental activation energy and standard deviation of 38.1 ± 0.5 kcal. per mole.

Ionic Strength Dependence.—One exchange measurement was obtained at 39.4° from a solution containing 0.0325 M U(VI), 0.00132 M U(IV) and 0.106 M hydrogen ion which was made up to an ionic strength of 0.57 with sodium perchlorate. From the observed exchange rate, a value of k = 8.49 × 10^{-6} M^2 sec.$^{-1}$ was calculated by means of equation 7, using the value of K_H = 0.0734 estimated for this solution from the data of Kraus and Nelson.[11]

Effect of Ultraviolet Irradiation.—A solution was made up containing 0.00132 M U(IV), 0.00484 M U(VI) and 0.214 M hydrogen ion at ionic strength 2.0. At room temperature this solution was expected to have a thermal exchange half-time greater than 1000 hr. Irradiation at 25.1° with the ultraviolet light source caused exchange to proceed with an observed half-time of 67.5 minutes, corresponding to a quantum yield for induced exchange of about 0.01. No measurable net oxidation or reduction of the uranium species present in the solution occurred during the irradiation.

Discussion

In order to attempt a quantitative correlation between the observed exchange reaction and the equilibrium represented by equation 1, it is necessary to know whether or not the U(V) ions formed in the equilibrium undergo exchange with U(VI)

$$U^*O_2^{++} + UO_2^+ \rightleftharpoons U^*O_2^+ + UO_2^{++} \quad (8)$$
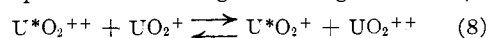
before disproportionating via the reverse of equation 1. The bimolecular rate constant for the exchange reaction 8 has been estimated from uranium exchange measurements[13] to lie between

(13) B. J. Masters and Harolyn K. Perkins, data presented before the Division of Inorganic Chemistry at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

the limits of 100 to 1000 M^{-1} sec.$^{-1}$, while a lower limit of 52 M^{-1} sec.$^{-1}$ has been deduced from recent measurements of the U(V)-catalyzed oxygen exchange between water and uranyl ion.[14] Under the conditions employed in the present study, the rapidity of reaction 8 in comparison with the equilibrium rate of U(V) disproportionation makes possible the simplifying assumption that the specific activities of the U(V) and U(VI) fractions are at all times equal. The experimentally measured exchange rate is then just one-half the equilibrium rate at which the reverse reaction in (1) is occurring, and we may write

$$\text{Rate of reverse reaction} = 2\,R_{xg}$$

with the understanding that the *net* rate of chemical change in the system is zero. By substituting equation 6 we obtain the relation

$$\text{Rate of reverse reaction} = 2k[\text{U}^{+4}][\text{UO}_2^{++}][\text{H}^+]^{-3} \quad (9)$$

The reverse step of equation 1 has been studied under conditions far from thermal equilibrium by Imai,[15] using the polarographic method. He has reported a rate dependence of the form
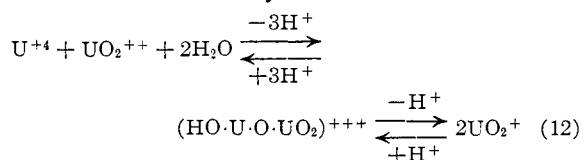
$$-\frac{\mathrm{d}}{\mathrm{d}t}[\text{UO}_2^+] = k_\text{D}[\text{UO}_2^+]^2[\text{H}^+] \quad (10)$$

in which the disproportionation rate constant k_D has the value 436 M^{-2} sec.$^{-1}$ for solutions of ionic strength 2 and at 25°. For similar solutions at thermal equilibrium, a value of $k = 2.13 \times 10^{-7}\,M^2$ sec.$^{-1}$ was observed in the present study, so that by equating equations 9 and 10

$$k_\text{D}/2k = [\text{U}^{+4}][\text{UO}_2^{++}]/[\text{UO}_2^+]^2[\text{H}^+]^4 = K_\text{E} \quad (11)$$

we obtain a value of 1.02×10^9 for the equilibrium constant, K_E. This result is in excellent agreement with the value of $K_\text{E} = 1.05 \times 10^9$ observed by Kraus and Nelson[7] in polarographic studies of the U(IV)–U(V)–U(VI) equilibrium at ionic strength 2.0 and 25°.

The foregoing result leaves little doubt that the activated complex encountered in the present study is identical with that formed in the U(V) disproportionation reaction, so that the net activation processes for these two reactions may be described schematically as

$$\text{U}^{+4} + \text{UO}_2^{++} + 2\text{H}_2\text{O} \underset{+3\text{H}^+}{\overset{-3\text{H}^+}{\rightleftharpoons}}$$

$$(\text{HO·U·O·UO}_2)^{+++} \underset{+\text{H}^+}{\overset{-\text{H}^+}{\rightleftharpoons}} 2\text{UO}_2^+ \quad (12)$$

in which the depicted intermediate represents the formula, but not necessarily the structure, of the activated complex.

For the aqueous UO_2^+ ion, standard thermochemical values of $\Delta H_f^0 = -247.4$ kcal. mole^{-1}, $\Delta F_f^0 = -237.6$ kcal. mole^{-1}, and $S^0 = 12$ e.u. have been quoted,[16] although a published reference is cited only for the ΔF_f^0 value. The available kinetic data for the reactions involved in (12) make possible an independent estimation of these quantities. For the forward reaction in (12)
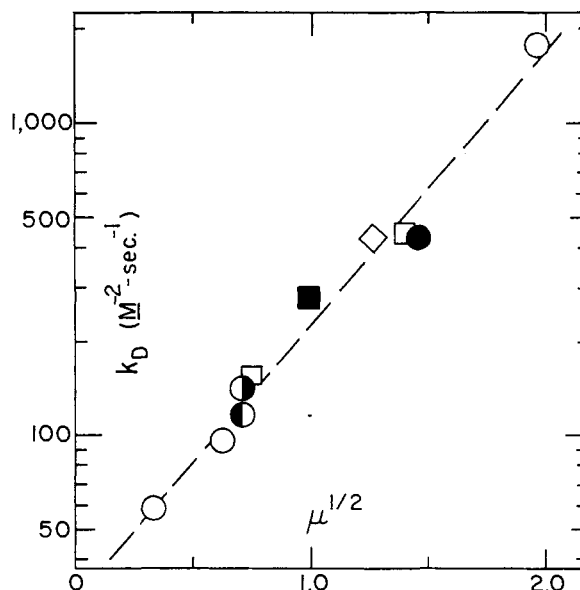

Fig. 2.—Effect of ionic strength upon the U(V) disproportionation rate constant, k_D, for perchlorate solutions. The values are calculated from the measurements of: O, Orlemann and Kern;[19] ◐, Duke and Pinkerton[20]; ◑, Koryta and Koutecky[21]; ●, Imai[15]; □, the present study together with the equilibrium data of Kraus and Nelson[7]; ■, Heidt[22] (solutions containing 0.2 M methanol); ◇, Gordon and Taube.[14]

the thermodynamic quantities of activation calculated in accordance with the absolute reaction rate theory[17] are $\Delta H^* = 37.5 \pm 0.5$ kcal. mole^{-1}, $\Delta F^* = 26.6 \pm 0.5$ kcal. mole^{-1} and $\Delta S^* = 36.4 \pm 1.6$ e.u. for solutions of ionic strength 2.0 at 25°. Bearing in mind that these quantities provide only approximations of the changes which would occur if the process were carried out in the hypothetical ideal state, we may add them to the standard thermochemical quantities[16] for the reactants on the left side of equation 12 to yield values of $\Delta H_f^0 = -496.2$ kcal. mole^{-1}, $\Delta F_f = -461.6$ kcal. mole^{-1} and $S^0 = -25.2$ e.u. for the activated complex. Subtracting the thermodynamic quantities of activation calculated[18] from Imai's data for the reverse reaction in (12) and dividing the results by two, one obtains values for UO_2^+ of $\Delta H^0 = -252.7$ kcal. mole^{-1}, $\Delta F^0 = -237.8$ kcal. mole^{-1} and $S^0 = -5$ e.u. Alternatively, these values may be obtained from the over-all equilibrium constants calculated by means of equation 11, without employing the assumptions involved in transition state theory.

From the observed ionic strength dependence of the forward step in reaction 12, together with the ionic strength dependence of K_E reported by Kraus and Nelson,[7] values of $k_\text{D} = 161$ and 446 M^{-2} sec.$^{-1}$ are estimated by means of equation 11 for 25° solutions of ionic strengths 0.57 and 2.0, respectively. These values, and the value of k_D inferred by Gordon and Taube[14] from measure-

(14) G. Gordon and H. Taube, *J. Inorg. Nuclear Chem.*, (1961).

(15) H. Imai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957).

(16) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

(17) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941, pp. 195–199.

(18) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

ments of the U(V)-catalyzed exchange of oxygen between U(VI) and water are plotted in Fig. 2, together with representative values of k_D calculated in accordance with the definition 10 from the best available previously reported data.[15,19-22] It is to be expected that the log k_D vs. $\sqrt{\text{ionic strength}}$ plot, employed here solely for convenience in presenting the data, should exhibit some deviation from linearity at the solute concentrations employed for these studies.

All of the values represented by circles in Fig. 2 were obtained by polarographic methods, either by following the time dependence of the U(V) oxidation wave diffusion current during the disproportionation of electrolytically prepared U(V) solutions,[19,20] or by measuring the limiting current for the reduction of U(VI) solutions at the dropping mercury electrode.[15,21] Some question may be raised as to the possible influence of the electrode surfaces upon the rates observed in both of these methods, particularly if the rate-determining step for the disproportionation involves a simple electron transfer. In the case of the latter method it has further been pointed out[19b] that the reaction occurring in the region of solution immediately surrounding the mercury droplet may not provide a fair representation of the disproportionation process in a continuous body of solution. However, as illustrated in Fig. 2, the close agreement of the disproportionation rate constants obtained by a variety of independent methods attests, at least in the present instance, to the validity of reaction rate measurements obtained by polarographic techniques. It perhaps should be pointed out that this confirmation does not apply quantitatively to the rate data obtained chronopotentiometrically, although U(V) disproportionation rates observed by this method[23] appear to be of the correct order of magnitude.

The reaction sequence represented by equation 12 appears to be formally identical with that encountered in reactions of other members of the actinide series. Hindman, Sullivan and Cohen have shown[24] that their observations of the Np(IV) +

Np(VI) → 2Np(V) reaction may be interpreted in terms of two paths, one of which exhibits a rate dependence of the form $[\text{Np}^{+4}][\text{NpO}_2^{++}][\text{H}^+]^{-3}$. They have also deduced, from studies of the Np(IV)-Np(V) exchange system,[25] the existence of a Np(V) disproportionation path with a rate dependence of the form $[\text{NpO}_2^+]^2[\text{H}^+]$. Although the plutonium analogue of the forward reaction in (12) has not been directly studied, the Pu(V) disproportionation reaction has been shown by Rabideau[26] to occur with a rate dependence of the form $[\text{PuO}_2^+]^2[\text{H}^+]$. Activated complexes with formulas differing from (12) only by one or two hydrogen ions have been reported for the neptunium system,[24,25] for the Am(V) disproportionation reaction system[27] and for the reaction systems U(IV)-Pu(VI)[28] and U(IV)-Np(VI).[29]

The pronounced effect of ultraviolet irradiation upon the U(IV)-U(VI) exchange rate observed in the present study is in qualitative agreement with the observations reported for sulfuric acid media by Betts.[4] Heidt[22] has studied the photolysis of U(VI) solutions in perchlorate media containing added methanol and reports quantum yields for U(IV) production of the order of tenths, the reaction presumably occurring via the photochemical formation of U(V) followed by disproportionation. The induced exchange effect observed in the present study can be explained by assuming that, in the absence of methanol, photolysis brings about an increase in the steady state concentration of U(V) without causing a net reduction of the solute. Further studies of the photochemically induced exchange reaction might prove useful for the elucidation of the mechanism of the uranyl oxalate actinometer.

(19) E. F. Orlemann and D. M. H. Kern: (a), *J. Am. Chem. Soc.*, **71**, 2102 (1949); (b) *ibid.*, **75**, 3058 (1953).

(20) F. R. Duke and R. C. Pinkerton, *ibid.*, **73**, 2361 (1951).

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