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A Uranium(V)–Uranium(VI) Complex and Its Effect on the Uranium(V) Disproportionation Rate[1]

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Spectrophotometric and kinetic evidence is given for the formation of a complex, $U_2O_4^{+3}$. The heat and entropy of formation from UO_2^+ and UO_2^{+2} were found to be -1.9 ± 0.3 kcal. mole^{-1} and -1 ± 1 cal. mole^{-1} deg.$^{-1}$ in perchlorate solutions 2.0 M in ionic strength. The complex has a characteristic absorption band at 7370 Å. (ϵ 27 M^{-1} cm.$^{-1}$). The disproportionation rate of the complex is much lower than that of UO_2^+, so U(V) solutions are greatly stabilized in the presence of U(VI). Rates of U(V) disproportionation were extrapolated to zero U(VI) to provide rate constants which are more reliable than previously available. Heats and entropies for the net activation process $2UO_2^+ + H^+ = [UO_2 \cdot UO_2 \cdot H^{+3}]^*$ were found to be 11.0 ± 0.4 kcal. mole^{-1} and -11.0 ± 1.5 cal. mole^{-1} deg.$^{-1}$.

Introduction

Binuclear cations have been shown to be important both as hydrolysis products[2] and as reaction intermediates.[3] Oxygenated cations such as the actinide "-yl" ions are particularly subject to this type of complexing, even in acid solutions. Sullivan[4] has shown that NpO_2^+ forms complexes with highly charged ions such as Cr^{+3}, Fe^{+3}, etc., as well as with UO_2^{+2}.

In this paper we report the formation of an analogous U(V)–U(VI) complex; association quotients were determined at various hydrogen ion concentrations and temperatures so that the heat and entropy of formation could be estimated.

Appreciable complexing between U(V) and U(VI) was first indicated by the observation that the rate of disproportionation of U(V) is greatly inhibited by U(VI). In addition, a convenient absorption band due to the complex was found; so both kinetic and the usual spectrophotometric measurements were used in determining the association quotients.

Previous determinations of U(V) disproportionation rates were based on polarographic measurements.[5] The present direct determinations of the rate have been extrapolated to zero U(VI) concentration for comparison with the earlier work.

Experimental

Reagents.—Stock solutions of $Eu(ClO_4)_3$ were prepared from pure Eu_2O_3 by dissolution in $HClO_4$ and recrystallization twice from water. Analysis was by the use of excess standard Ce(IV) after complete reduction on Zn amalgam. Analysis for free acid was by titration with standard NaOH after removal of the Eu as the oxalate.

Stock solutions of $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ were prepared by the neutralization of their carbonates with $HClO_4$ followed by two crystallizations from water. The trace of free acid remaining was determined by titration, and the total ClO_4^- by the use of a cation-exchange resin. Solutions of $UO_2(ClO_4)_2$, $LiClO_4$, $NaClO_4$, $HClO_4$, and the redistilled water were prepared and analyzed as before.[6] The salts were all recrystallized twice from water.

Solutions of U(V) perchlorate were prepared by reducing U(VI) with Eu(II) which had been made by reducing Eu(III) on Zn amalgam. Preliminary experiments[7] showed that Eu(II) reacts rapidly with U(VI) in perchloric acid but only slowly with U(V). The apparent second-order rate constant for the former reaction is about 2×10^3 M^{-1} sec.$^{-1}$ at 0° in 0.1 M $HClO_4$. Solutions of U(V) were also prepared by adding U(III)–U(IV) mixtures to U(VI) in 0.03 M $HClO_4$.[8] The mixtures were made by reducing U(VI) on Zn amalgam. In runs at 25° in 0.2 M U(VI) and 0.275 M $HClO_4$ these preparations were found to be indistinguishable from those made using Eu(II). The concentration units used in this paper are moles per liter (M) at 23°.

Procedure.—Spectrophotometric measurements were made with a Cary recording spectrophotometer equipped with a small water-filled thermostat in the light beam. Appropriate amounts of U(VI), acid, and salt, usually 65 ml., were placed in the cell, which was swept with argon and brought to temperature in the thermostat. Reaction was started by injecting 2.0 ml. of Eu(II), prepared at the proper temperature, by means of a hypodermic syringe with a Teflon needle. Complete stirring was obtained within 2 sec. by means of a Teflon-covered stir bar in the bottom of the cell. After completion of the reaction, excess standard Ce(IV) was pipetted into the cell and the total reducing agent was determined by back titration with standard Fe(II).

Catalytic Impurities.—The use of commercial $HClO_4$ or of $UO_2(ClO_4)_2$, $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, or $Eu(ClO_4)_3$ which had been given additional recrystallizations gave essentially the same results as the use of the reagents described above. Zn(II) from the amalgam was shown to be without effect. Both Eu(II) and U(V) are very sensitive to O_2 from the air; so all solutions and absorption cells were thoroughly swept with purified argon before and during the runs. Many reactions of uranium are affected by light, so rates were compared in the presence and absence of the intense white light of the infrared source in the spectrophotometer. The results were the same within the experimental error; the light caused an increase in rate of no more than 3%.

Results

The Spectrum of the U(V)–U(VI) Complex.—A solution was prepared at 0° which was 0.0013 M U(V) (from Eu(II)), 0.10 M U(VI), 0.10 M $HClO_4$, and 1.6 M

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[1] Work done under the auspices of the U. S. Atomic Energy Commission.

[2] Numerous papers by L. G. Sillén and co-workers; see, for example, *Acta Chem. Scand.*, **17**, 2644 (1963).

[3] T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964), and the references cited there.

[4] J. C. Sullivan, *ibid.*, **3**, 315 (1964), and the references cited there.

[5] (a) H. Imai, *Bull. Chem. Soc. Japan*, **30**, 873 (1957); (b) J. Koryta and J. Koutecky, *Collection Czech. Chem. Commun.*, **20**, 423 (1955); (c) D. M. H. Kern and E. F. Orelman, *J. Am. Chem. Soc.*, **71**, 2102 (1949).

[6] T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **69**, 176 (1965).

[7] H. Taube and T. W. Newton, unpublished observations.

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

$LiClO_4$. A spectrophotometric scan from 9000 to 7000 Å. showed the presence of an absorption band with λ_{max} 7370 Å. and a half-width of about 550 Å. Possible absorption in the region from 7000 to 3500 Å. is almost completely obscured by that of U(IV) and U(VI). However, some indication of additional absorption near 4000 Å. was obtained. The band at 7370 Å. was observed to disappear as the U(V) disproportionated. Apparent second-order rate constants calculated from this disappearance were in good agreement with those determined from the growth of the U(IV) band at 6478 Å. This shows that the absorbance at 7370 Å. is proportional to the U(V) concentration when the U(VI) concentration is large.

Comparison of Rates with Previous Work.—Sets of rate runs were made in $NaClO_4$ solutions at 25.1° to determine whether the present direct spectrophotometric method gives results in agreement with previous polarographic determinations. The agreement is satisfactory at 25° as is shown in Table I.

TABLE I

U(V) DISPROPORTIONATION RATES BY SPECTROPHOTOMETRY AND BY POLAROGRAPHY; $HClO_4$–$NaClO_4$ SOLUTIONS AT 25.1°

$-d[U(V)]/dt = k'[U(V)]^2$

	Spectrophotometric	Polarographic
Ionic Strength 2.1 M		
$[HClO_4]$, M	0.10	0.10
$[U(VI)]_0$, 10^3 M	4.0	4.0
$[U(V)]_0$, 10^3 M	2.0	. . .
No. of detn.	6	8
Av. $k'/[H^+]$, M^{-2} sec.$^{-1}$	416[a]	435[b]
Mean deviation	11	18
Ionic Strength 0.5 M		
$[HClO_4]$, M	0.05	0.1–0.5
$[U(VI)]_0$, 10^3 M	8.0	8.0
$[U(V)]_0$, 10^3 M	2.0	. . .
No. of detn.	6	4
Av. $k'/[H^+]$, M^{-2} sec.$^{-1}$	129[a]	143[c]
Mean deviation	1	. . .

[a] This work. [b] Reference 5a. [c] Reference 5b.

Gordon and Taube[9] have shown that U(V) catalyzes the oxygen exchange between U(VI) and H_2O. An estimate of the disproportionation rate constant was obtained from the decrease in exchange rate in solutions initially containing U(V). A value of 435 M^{-1} sec.$^{-1}$ was found at 25° for a solution of 0.5 M $UO_2(ClO_4)_2$ and 0.0811 M $HClO_4$. Our results indicate that this value is too high by a factor of about 10. The high value probably was caused by air oxidation of U(V) from the start of the experiment and not merely after four half-lives had elapsed, as was originally suggested.

Effect of Various Cations.—Most of the experiments for this paper were concerned with the effect of the concentration of uranium(VI), [U(VI)], on the absorption attributed to the complex and on the rate of disproportionation of U(V). These experiments were done at constant ionic strength and at essentially constant ionic environment in that UO_2^{+2} was substituted for Mg^{+2} such that the sum of their concentrations was constant at 0.20 M. In this connection, an experiment was done to determine the effect of various cations on the rate at constant ionic strength. The solutions were 1.10 M $LiClO_4$, 0.60 M $HClO_4$, 0.006 M U(VI), 0.0017 M U(V), and sufficient added salt to make the ionic strength 2.00 M. The relative values of the apparent second-order rate constants at 0.3° were: $LiClO_4$, 1.00; $Mg(ClO_4)_2$, 0.95; $Zn(ClO_4)_2$, 0.95; $Ba(ClO_4)_2$, 0.92; and $La(ClO_4)_3$, 0.89. Substituting 1.30 M $NaClO_4$ for 1.30 M $LiClO_4$ at 25° was found to decrease the rate of disproportionation by (15 ± 3)%; in this experiment $[H^+]$ was 0.10 M and μ was 2.00 M.

Effect of Chloride Ion.—Imai's[5a] data show that increasing the $[Cl^-]$ from zero to 0.20 M increases the rate by a factor greater than 2 in a solution which was 0.10 M in $HClO_4$ and 2.0 M in $NaClO_4$ at 25°. We have duplicated these conditions and find that the rate increases by only about 28%. It would seem that one or more of the assumptions involved in the interpretation of the polarographic data is not valid in chloride solutions.

The effect of 0.10 M Cl^- on the formation of the U(V)–U(VI) complex was found to be rather small. At 0° in 0.40 M $HClO_4$ at an ionic strength of 2.0 M the apparent association quotient was found to be only about 13% less than in the absence of Cl^-.

Effect of Hydrogen Ion and Temperature.—Sets of runs at various $[H^+]$ and temperatures were made to determine the effect of [U(VI)] on the absorption at 7370 Å. and on the rate of disproportionation of U(V). The absorption at 7370 Å. was extrapolated to the time of mixing with the aid of the second-order rate constants determined on identical solutions. The average absorption coefficients, ϵ, determined in this way are given in Table II. At all temperatures and $[H^+]$ the values increase with increasing [U(VI)].

The change in absorbance with time was in good agreement with a second-order rate law. The wave length used was usually 6478 Å., an absorption maximum for U(IV), but occasionally 7370 Å. was used. The reaction was followed to about 90% completion and the apparent second-order rate constants, $k' = (-d[U(V)]/dt)/[U(V)]^2$, were determined using a nonlinear least-squares program based directly on the absorbance readings. The rate constants obtained are given in Table III. The values decrease markedly with increase in [U(VI)]. During the course of the disproportionation [U(VI)] increases, so k' cannot be expected to remain strictly constant during an individual run. This variation was not detectable and average values were determined. Calculations based on eq. 5 (below) showed that under our experimental conditions the effective [U(VI)], which corresponds to the average k' during the run, is given by $[U(VI)]_0 + 0.34[U(V)]_0$.

Interpretation and Discussion

Ionic Species.—In acidic solutions U(V) and U(VI) are predominantly UO_2^+ and UO_2^{+2}. Hydrolysis of

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[9] G. Gordon and H. Taube, *J. Inorg. Nucl. Chem.*, **16**, 272 (1961).

Table II

Average Absorption Coefficients, 7370 Å.

Units are M^{-1} cm.$^{-1}$

(0.3°)

U(VI), M x 10³	$[H^+]$ M			
	0.10	0.40	0.70	1.00
2.08	2.1	1.8	1.7	1.9
8.73	5.0	4.9	4.4	4.4
18.1	8.1	7.9	7.5	6.9
38.0	13.1	12.7	11.8	11.6
78.1	17.4	17.3	-	16.0
91.4	-	-	17.8	-
131	-	-	-	19.3
198	22.3	22.0	21.6	22.0

(13.8°)

	0.10	0.20	0.40	0.60
2.08	1.8	1.8	1.9	2.2
8.74	4.7	4.2	4.2	4.1
18.1	7.4	7.2	7.2	6.3
38.1	11.6	11.4	10.9	10.6
78.1	16.3	16.2	15.7	15.2
131	19.7	19.4	18.9	18.7
198	21.4	21.5	20.8	20.7

(25.1°)

	0.050	0.10	0.20	0.40
2.08	2.0	1.6	1.6	1.7
"	1.7			2.1
8.73	4.5	4.1	4.6	3.8
"	4.2			3.8
18.1	7.2	6.8	-	5.9
"	6.9			
38.0	11.0	10.8	10.2	10.4
	10.8			
78.1	-	-	15.1	14.8
"				14.0
91.4	16.6	16.1	-	-
"	16.1			
105	17.4	-	-	-
131	19.1	-	18.5	17.8
"				18.0
198	21.3	20.5	20.4	20.0
"	21.0			20.3

Table III

Apparent Second-Order Rate Constants

Units are M^{-1} sec.$^{-1}$

(0.3°)

U(VI), M x 10³	$[H^+]$ M			
	0.10	0.40	0.70	1.00
2.77	8.25	28.8	45.8	61.0
9.43	6.28	22.3	36.5	46.1
18.8	4.60	16.7	26.2	32.6
38.8	2.81	10.1	16.4	22.2
78.7	1.54	4.86	-	10.9
92.1	-	-	6.65	-
132	-	-	-	5.66
199	0.51	1.42	2.28	3.14

(13.8°)

	0.10	0.20	0.40	0.60
2.77	22.2	43.3	69.8	100
9.43	17.3	-	59.1	81.2
18.8	14.0	24.4	45.5	59.3
38.8	9.21	16.2	29.6	41.1
78.7	4.97	8.64	15.5	21.8
132	3.07	4.86	8.33	12.0
199	1.90	2.91	4.76	6.7

(25.1°)

	0.050	0.10	0.20	0.40
2.76	27.7	46.1	86.1	135
"	26.8			
9.42	21.2	40.4	81.1	126
"	22.5			114
18.7	18.3	32.2	54.0	81
"	18.3			103
38.8	12.8	21.1	37.2	64.8
"				68.6
78.7	8.41	-	20.8	37.1
"				35.1
92.0	7.35	10.7	-	-
105	6.48	-	-	-
132	6.33	-	12.8	21.3
"				21.6
199	4.87	5.14	7.93	12.6
"	4.74			13.0

UO_2^+ is probably very slight.[10] Hydrolysis of UO_2^{+2} gives predominantly $(UO_2)_2(OH)_2^{+2}$ with an association quotient of about 10^{-6} M at an ionic strength of 3.0 M. The formation of this species is thus negligible even for 0.2 M UO_2^{+2} in 0.05 M $HClO_4$.[2]

Complex Formation.—The effect of [U(VI)] on the average absorption coefficient (ϵ = (total absorbance)/(path)[U(V)]) and on the rate of disproportionation is most readily explained in terms of a U(V)–U(VI) complex which absorbs at 7370 Å. and disproportionates much more slowly than UO_2^+

$$\mathrm{U(V)} + \mathrm{U(VI)} = \mathrm{U_2(XI)}$$
$$\beta = [\mathrm{U_2(XI)}]/[\mathrm{U(V)}][\mathrm{U(VI)}] \qquad (1)$$

$$2\mathrm{U(V)} = \mathrm{U(IV)} + \mathrm{U(VI)}$$
$$-\mathrm{d}[\mathrm{U(V)}]/\mathrm{d}t = k_1'[\mathrm{U(V)}]^2 \qquad (2)$$

$$\mathrm{U(V)} + \mathrm{U_2(XI)} = \mathrm{U(IV)} + 2\mathrm{U(VI)}$$
$$-\mathrm{d}[\mathrm{U(V)}]/\mathrm{d}t = k_2[\mathrm{U(V)}][\mathrm{U_2(XI)}] \qquad (3)$$

In these equations [U(V)] and [U(VI)] represent the sums of the concentrations of all monomeric forms. This scheme leads to an average absorption coefficient given by

$$\bar{\epsilon} = (\epsilon_0 + \epsilon_1\beta[UO_2^{+2}])/(1 + \beta[UO_2^{+2}]) \qquad (4)$$

and an apparent second-order rate constant given by

$$k' = (k_1' + k_2\beta[UO_2^{+2}])/(1 + \beta[UO_2^{+2}])^2 \qquad (5)$$

These equations fit the data at constant [H$^+$] and temperature very well. For example, a least-squares treatment of the absorption data in Table II for 0.3° and 0.10 M $HClO_4$ gives $\epsilon_0 = 0.8 \pm 0.2$ M^{-1} cm.$^{-1}$, $\epsilon_1 = 27.2 \pm 0.5$ M^{-1} cm.$^{-1}$, and $\beta = 22.1 \pm 1.3$ M^{-1}; these parameters reproduce the data with a mean deviation of 0.003 and a maximum deviation of 0.006 absorbance unit. A similar treatment of the analogous rate data gives $k_1' = 9.1 \pm 0.3$ M^{-1} sec.$^{-1}$, $k_2 = 1.8 \pm 0.4$ M^{-1} sec.$^{-1}$, and $\beta = 24.3 \pm 2.0$ M^{-1}; these give a mean deviation of 1.8% and a maximum deviation of 4%. The proposed reaction scheme is strongly supported by the fact that the two values found for β agree with each other within one standard deviation, the indicated uncertainty. Similar agreement was obtained with the other data sets. Since eq. 4 and 5 are sufficient to describe the data, there is no evidence for higher complexes.

For further calculations the absorbance and rate data were combined and it was assumed that the best values of β are the ones which best reproduce both types of data simultaneously. The uncertainty in absorbance and the per cent uncertainty in the rate constants were assumed to be constant; an error of 0.005 in the former was considered just as likely as an error of 5% in the latter. In order to make these calculations an appropriate subroutine was written for the general nonlinear least-squares program for the IBM-7094 in use at Los Alamos.[11] The results of these calculations are summarized in Table IV.

Table IV

Values of the Parameters at Various [H$^+$] and Temperatures

Temp., °C.	[HClO$_4$], M	β, M^{-1}	ϵ_0, M^{-1} cm.$^{-1}$	ϵ_1, M^{-1} cm.$^{-1}$	k_1', M^{-1} sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$	k_1'/[H$^+$], M^{-2} sec.$^{-1}$
0.3	0.100	22.5 ± 1.0	0.8 ± 0.2	27.0 ± 0.3	8.9 ± 0.2	1.5 ± 0.2	89 ± 2
	0.400	21.6 ± 0.5	0.6 ± 0.1	27.1 ± 0.2	32.3 ± 0.5	1.8 ± 0.4	81 ± 1
	0.700	19.4 ± 0.5	0.7 ± 0.1	27.2 ± 0.2	50 ± 1	0.6 ± 0.6	72 ± 1
	1.00	16.7 ± 1.0	0.85 ± 0.25	28.0 ± 0.6	61 ± 2	−1 ± 2	61 ± 2
13.8	0.100	18.4 ± 0.7	0.9 ± 0.1	27.2 ± 0.3	23.6 ± 0.4	4.8 ± 0.6	236 ± 4
	0.200	17.3 ± 1.6	0.8 ± 0.4	27.6 ± 0.8	40.5 ± 1.9	4.9 ± 2.2	202 ± 9
	0.400	16.5 ± 0.4	1.1 ± 0.1	27.0 ± 0.2	77.4 ± 1.0	3.1 ± 1.1	193 ± 3
	0.600	14.5 ± 0.8	1.2 ± 0.2	27.6 ± 0.5	102 ± 3	0 ± 3	171 ± 5
25.1	0.050	16.5 ± 1.2	1.0 ± 0.2	27.0 ± 0.8	27.0 ± 0.8	15 ± 2	541 ± 16
	0.100	16.7 ± 0.7	0.9 ± 0.1	26.3 ± 0.3	50.4 ± 0.9	13 ± 1	504 ± 9
	0.200	16.8 ± 2.0	1.1 ± 0.4	26.1 ± 0.9	94 ± 5	16 ± 7	470 ± 26
	0.400	13.1 ± 1.3	0.9 ± 0.3	27.6 ± 1.0	141 ± 6	9 ± 9	352 ± 16

Hydrogen Ion and Temperature Dependence.—The fact that β decreases only moderately as [H$^+$] increases shows that the equilibrium represented by eq. 1 is predominantly as shown in eq. 6.

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[10] J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co., Ltd., London, 1957 (also, John Wiley and Sons, Inc., New York, N. Y.), Chapter V.

[11] This program is based on R. H. Moore and R. K. Zeigler, Los Alamos Scientific Laboratory Report, LA-2367, Oct. 1959, available from the Office of Technical Services, U. S. Department of Commerce, Washington, D. C., $2.25. We thank Dr. Moore for helpful advice on writing the subroutine.

TABLE V

VALUES OF THE PARAMETERS FOR VARIOUS COMBINATIONS OF EQ. 7–11

	Combination of functions					
	1 (7), (9)	2 (7), (10)	3 (7), (10*)[a]	4 (7), (11)	5 (8), (11)	6 (8*),[b] (11)
ΔS_β, cal. mole^{-1} deg.$^{-1}$	0 ± 0.8[c]	−0.6 ± 1.1	−0.7 ± 1.0	−0.1 ± 0.8	0.2 ± 0.8	−0.9 ± 0.7
ΔH_β, kcal. mole^{-1}	−1.7 ± 0.2	−1.9 ± 0.3	−1.9 ± 0.3	−1.7 ± 0.2	−1.6 ± 0.2	−1.9 ± 0.2
b, M^{-1}	−0.23 ± 0.03	−0.18 ± 0.03	−0.19 ± 0.03	−0.23 ± 0.03	...	−0.1[d]
α_b, deg.$^{-1}$ × 10^2	4.3 ± 1.2	4.6 ± 2.0	4.1 ± 1.7	4.3 ± 1.2	...	0[d]
ΔS_K, cal. mole^{-1} deg.$^{-1}$	...	...	...	...	−23.9 ± 5.6	−17 ± 8
ΔH_K, kcal. mole^{-1}	...	...	...	...	−4.4 ± 1.6	−2.4 ± 2.1
ΔS_1^*, cal. mole^{-1} deg.$^{-1}$	−10.1 ± 0.7	−12.8 ± 0.9	−13.7 ± 0.8	−9.6 ± 0.8	−9.3 ± 0.9	−9.6 ± 0.9
ΔH_1^*, kcal. mole^{-1}	11.1 ± 0.2	10.6 ± 0.3	10.3 ± 0.2	11.2 ± 0.2	11.3 ± 0.3	11.3 ± 0.2
d, M^{-1}	−0.39 ± 0.04	...	−0.1[d]	...	...	...
α_d, deg.$^{-1}$ × 10^2	6.2 ± 1.2	...	0[d]	...	...	...
ΔS_0^*, cal. mole^{-1} deg.$^{-1}$	...	−27.2 ± 3.7	−23.9 ± 4.3	−32.6 ± 2.6	−33.7 ± 3.6	−32.7 ± 3.1
ΔH_0^*, kcal. mole^{-1}	...	8.4 ± 1.1	9.4 ± 1.2	4.6 ± 0.8	4.2 ± 1.0	4.5 ± 0.9
ϵ_1^0, M^{-1} cm.$^{-1}$	27.2 ± 0.2	27.2 ± 0.2	27.2 ± 0.2	27.2 ± 0.2	27.2 ± 0.2	27.2 ± 0.2
$\alpha_{\epsilon 1}$, deg.$^{-1}$ × 10^4	−8 ± 4	−5 ± 5	−5 ± 5	−8 ± 4	−10 ± 5	−9 ± 4
ϵ_0^0, M^{-1} cm.$^{-1}$	0.8 ± 0.1	0.7 ± 0.1	0.7 ± 0.1	0.8 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
$\alpha_{\epsilon 1}$, deg.$^{-1}$ × 10^4	1 ± 1	1 ± 1	1 ± 1	1 ± 1	1 ± 1	1 ± 1
ΔS_2^*, cal. mole^{-1} deg.$^{-1}$	−2 ± 3	−5 ± 4	−5 ± 4	−2 ± 3	−0.4 ± 4	−1 ± 3
ΔH_2^*, kcal. mole^{-1}	15.6 ± 0.9	14.8 ± 1.2	14.9 ± 1.1	15.7 ± 0.9	16.1 ± 1.1	15.9 ± 1.0
Weighted variance × 10^3	2.19	3.40	2.98	2.13	3.16	2.64

[a] Equation 10 multiplied by a Harned term. [b] Equation 8 multiplied by a Harned term. [c] The uncertainties in this table are estimates of the standard deviations. [d] Arbitrarily fixed.

$$UO_2^+ + UO_2^{+2} = U_2O_4^{+3}$$
$$\beta_0 = [U_2O_4^{+3}]/[UO_2^{+2}][UO_2^+] \qquad (6)$$

The apparent second-order rate constant for the disproportionation of uncomplexed U(V), k_1', increases with both temperature and $[H^+]$, as expected. Previous polarographic results indicate that $k'/[H^+]$[5a,b] or k'/a_{H^+} is essentially constant. The present direct determinations, extrapolated to zero [U(VI)], show an appreciable decrease in $k_1'/[H^+]$ with increasing $[H^+]$ at all three temperatures.

The substitution of H^+ for Li^+ at constant ionic strength may be expected to have an effect even on reactions among positive ions. The available evidence suggests that such medium effects are not large, perhaps 10%/M.[12] Medium effects as well as chemical effects may contribute to an observed $[H^+]$ dependence and although it may not be possible to exclude one or the other, it is important to determine whether either effect alone is sufficient to explain the observations.

For these reasons the following functional forms were considered

$$\beta = \beta_0 \exp(b[H^+]) \qquad (7)$$

$$\beta = \beta_0(1 + K/[H^+]), \text{ where } K = [U_2O_5H^{+2}][H^+]/[U_2O_4^{+3}] \qquad (8)$$

$$k_1' = k_1[H^+] \exp(d[H^+]) \qquad (9)$$

$$k_1' = k_0 + k_1[H^+] \qquad (10)$$

$$k_1' = [(1/k_0) + (1/k_1[H^+])]^{-1} \qquad (11)$$

Equation 7 represents a medium effect governed by Harned's rule,[13] and eq. 8 represents a chemical effect, the hydrolysis of the complex. In eq. 9 the lack of constancy in $k_1'/[H^+]$ is attributed to a medium effect; eq. 10 represents a mechanism with parallel paths and eq. 11 one with consecutive reactions. Plots of the appropriate functions of β or k' vs. $[H^+]$ showed that eq. 7–11 can reproduce these quantities fairly well at any of the experimental temperatures.

To determine whether any of these possibilities could be excluded, various combinations of the functions were used to fit all of the experimental $\bar{\epsilon}$ and k' values simultaneously. The usual temperature dependences were assumed.

$$\epsilon_i = \epsilon_i^0(1 + \alpha_{\epsilon i}t),\ b = b_0(1 + \alpha_b t), \text{ etc.} \qquad (12)$$

$$\beta = \exp(\Delta S_\beta/R) \exp(-\Delta H_\beta/RT) \qquad (13)$$

$$k_i = 2(kT/h) \exp(\Delta S_i^*/R) \exp(-\Delta H_i^*/RT) \qquad (14)$$

In these expressions the α's are the indicated temperature coefficients, t is the temperature (°C.), and the other symbols have their usual significance. The factor of 2 in the absolute reaction rate theory expression is required to make the ΔS^* values consistent with the net activation processes to be given later. The values of the parameters which best reproduce all of the data were found using the nonlinear least-squares program mentioned above. The results for various assumptions are summarized in Table V.

The simplest interpretation of the data is in terms of eq. 7 and 9; the resulting values of the parameters are listed in the first column of the table. The 90 absorbance values were reproduced with a mean deviation of 0.003 using the tabulated values of the appropriate eight parameters. It is to be noted that the temperature coefficients of the absorption coefficients are not significant, so essentially as good fits could have been obtained using only six parameters. The 92 observed rate constants were reproduced with a mean deviation of 3.4% using the tabulated values of the appropriate ten parameters. This particular mathematical model

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(12) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(13) See, for example, R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, Chapter 15.

TABLE VI

CATION–CATION INTERACTIONS

Process	β (25°), M^{-1}	ΔH, kcal. mole^{-1}	ΔS, cal. mole^{-1} deg.$^{-1}$	μ, M	Ref.
$UO_2^+ + UO_2^{+2} = U_2O_4^{+3}$	16	-1.9 ± 0.3	-1 ± 1	2.0	This work
$NpO_2^+ + UO_2^{+2} = NpUO_4^{+3}$	0.7	...	...	3.0	14
$Cr^{+3} + NpO_2^+ = CrNpO_2^{+4}$	2.6	-3.3 ± 0.6	-9.0 ± 1.9	8.0	4
$2UO_2OH^+ = (UO_2)_2(OH)_2^{+2}$	$\sim 3 \times 10^5$	-12 ± 4	-15 ± 10	0.5	15
$2InOH^{+2} = In_2(OH)_2^{+4}$	$\sim 4 \times 10^3$	1 ± 2	18 ± 6	3.0	16
$2ThOH^{+3} = Th_2(OH)_2^{+6}$	$\sim 2 \times 10^3$	3	27	1.0	17
$Th^{+4} + Th(OH)_2^{+2} = Th_2(OH)_2^{+6}$	$\sim 2 \times 10^3$	0.9	17	1.0	17
$2FeOH^{+2} = Fe_2(OH)_2^{+4}$	$\sim 10^3$	-28 ± 5	-80 ± 17	3.0	18

thus reproduces the data within the experimental error and appears to be satisfactory except for the values required for the Harned coefficients and their temperature coefficients. These require that β decrease by factors of 1.25 and 1.60 and $k_1'/[H^+]$ decrease by factors of 1.48 and 2.71 at 0 and 25°, respectively, when 1 M $HClO_4$ is substituted for 1 M $LiClO_4$ at constant ionic strength. These factors are abnormally large,[12] so other possibilities were tried also.

The assumption of rate law (10) in place of (9) leads to a distinctly poorer fit of the data, as shown in the second column of the table. As might be expected, this can be improved slightly by combining a reasonable medium effect with the postulated mechanism (column 3).

The participation of binuclear intermediates in consecutive reactions has been indicated for other systems,[3] so this possibility was tested here. An example of such a mechanism is

$$2UO_2^+ = U_2O_4^{+2}$$

$$d[U_2O_4^{+2}]/dt = k_f[UO_2^+]^2 - k_r[U_2O_4^{+2}] \qquad (15)$$

$$U_2O_4^{+2} + H^+ = \text{products}$$

$$-d[U_2O_4^{+2}]/dt = k_c[U_2O_4^{+2}][H^+] \qquad (16)$$

The steady-state approximation for $[U_2O_4^{+2}]$ leads to rate law (11). As shown in column 4, the use of this assumption leads to a fit which is slightly better than that from (9). It thus appears likely that the disproportionation of U(V) involves a binuclear intermediate, but the other possibilities cannot be considered disproved.

Hydrolysis of the complex, eq. 8, was considered as an alternative to the medium effect described by eq. 7. The results, in column 5, show that this assumption leads to a poorer fit of the data, but probably not outside the experimental error. The assumption of eq. 8, modified by a reasonable medium effect, together with eq. 11, appears to be a satisfactory compromise between the best fit of the data and chemical plausibility.

Heats and Entropies of Association.—In spite of the various possibile interpretations of the $[H^+]$ dependences discussed above, it is clear that the predominant association equilibrium is (6), for which $\Delta H = 1.9 \pm 0.3$ kcal. mole^{-1} and $\Delta S = -1 \pm 1$ cal. mole^{-1} deg.$^{-1}$ in solutions of ionic strength 2.0 M from 0 to 25°. The small value for ΔS suggests a loose structure for the complex together with a rather wide distribution of the net charge.

The small amount of information apparently available on cation–cation interaction is summarized in Table VI; some values for hydrolytic dimers have been included for comparison. Published values for ΔH and ΔS are available for the processes $M^{+n} + H_2O = MOH^{+n-1} + H^+$ and $2M^{+n} + 2H_2O = M_2(OH)_2^{+2n-2} + 2H^+$ where M is U(VI),[15] In(III),[16] Th(IV),[17] and Fe(III).[18] For Table VI, the values for the two hydrolysis processes were combined to give those for the dimerizations listed. It is seen that the hydrolytic dimers are much more stable with respect to dissociation than are the dimers of the actinide "-yl" ions. The entropy values for the association of these latter ions are more negative than the ones for Th(IV) and In(III), but are perhaps more positive than for U(VI) as UO_2OH^+. There is evidence for $CrUO_2^{+4}$,[19] analogous to $CrNpO_2^{+4}$, but no information is available on its dissociation into Cr^{+3} and UO_2^+.

Heats and Entropies of Activation.—The most important net activation process involved in the disproportionation of U(V) is

$$2UO_2^+ + H^+ = [UO_2 \cdot UO_2 \cdot H^{+3}]^*$$

The apparent values for the thermodynamic quantities of activation for this process depend somewhat on which mechanism is favored; average values are $\Delta H^* = 11.0 \pm 0.4$ kcal. mole^{-1} and $\Delta S^* = -11.0 \pm 1.5$ cal. mole^{-1} deg.$^{-1}$. These values are not in agreement with the previously reported ones which were $\Delta H^* = 10.2$ kcal. mole^{-1} and $\Delta S^* = -17.1$ cal. mole^{-1} deg.$^{-1}$.[3] The exact reason for this discrepancy is not known, but it should be noted that the polarographic temperature dependence data interpolated to 25° are in very poor agreement with the polarographic $[H^+]$ dependence data at 25°.

A minor path for the disproportionation of U(V) in the presence of U(VI) involves the reaction between UO_2^+ and $U_2O_4^{+3}$; the uncertainties with respect to this path are such that thermodynamic quantities of activation should not be quoted.

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(14) J. C. Sullivan, J. C. Hindman, and A. J. Zielen, *J. Am. Chem. Soc.*, **82**, 5288 (1960).

(15) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).

(16) K. Schlyter, *Trans. Roy. Inst. Tech., Stockholm*, No. 182 (1961).

(17) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, *Inorg. Chem.*, **4**, 518 (1965).

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(19) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **1**, 368 (1962).