be −0.29 ± 0.07 Å. The calculated r_{max} for the $6p_{3/2}$ outermost shell of No^{2+} is 0.74 Å and $\langle r \rangle$ is 0.84 Å. The No^{2+} outermost shell of $6p_{3/2}$ is the same as that of Ra^{2+} As we have shown, No^{2+} behaves chemically in a manner similar to the alkaline earths. It is therefore reasonable to suppose that the Δ's derived from the alkaline earths apply to No^{2+} as well. In this way, the ionic radius is calculated to be 1.1 Å in agreement with our results from solvent extraction and ion exchange.

As can be seen in Table I, although both No^{2+} and Ra^{2+} have the same outer shell, the radius of No^{2+} is much smaller. A similar situation is found in the comparison of Yb^{2+}, the lanthanide analog of No^{2+}, and Ba^{2+}. Beck and Barnighausen[19] give 1.03 Å as the ionic radius of Yb^{2+} for six-coordination, a value in the range of our No^{2+} value.

Our value for the ionic radius can be used to calculate the single-ion heat of hydration of the No^{2+} ion using an empirical form of the Born equation given by Phillips and Williams[20a]

$$H_{hyd} = -\frac{7.32z^2}{r + 0.85}\ \text{eV} \qquad (1)$$

The value of the constant is obtained as 7.32 ± 0.08 for the alkaline earths using the values of H_{hyd} given by Phillips and Williams.[20b] This equation is found by these authors to give the single-ion hydration energies accurately for many ions including the alkali metals, the alkaline earths, Al^{3+}, Fe^{3+}, and Y^{3+}, among others. It is therefore reasonable to suppose that eq 1 will give an accurate value for No^{2+}. The value so calculated is −355 kcal (g-atom)$^{-1}$ compared to −373 for Ca^{2+} and −338 for Sr^{2+}.

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Registry No. No^{2+}, 30927-24-3.

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Kinetics and Mechanism of the Disproportionation of Uranium(V)

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The kinetics and mechanism of the disproportionation of U(V) have been investigated. In agreement with a previous study (T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965)), the rate of disproportionation was observed to be retarded by the presence of U(VI), the effect being attributed to the formation of a $U^V \cdot U^{VI}$ complex whose absorption spectrum in the range 360–760 nm has been measured. The effect of ionic strength, acid concentration, and the presence of complexing anions on the disproportionation rate has been examined. The reaction has also been studied in D_2O solution and reaction mechanisms are discussed.

Introduction

The kinetics and mechanism of the U(V) disproportionation reaction (eq 1) have been the subject of numerous in-

$$2UO_2^{+} + 4H^+ \rightarrow U^{4+} + UO_2^{2+} + 2H_2O \qquad (1)$$

vestigations,[1] the reaction rate usually being measured by electrochemical methods. Although there is considerable variation in the values of the reported rate constants, there has been general agreement that the reaction is second order with respect to the U(V) concentration and positive first order with respect to the acid concentration. The rate constant for the disproportionation was found[1d] to be noticeably higher in D_2O solution compared to that observed in H_2O, this observation being interpreted as indicating that the proton-transfer mechanism originally proposed by Kern and Orlemann[1a,b] was probably not applicable.

In the first study of the disproportionation using direct spectroscopic techniques, Newton and Baker[2] observed that the rate of the disproportionation decreased with increasing U(VI) concentration. This effect was attributed to the formation of a $U^V \cdot U^{VI}$ binuclear complex, and the authors were able to identify an absorption band at 737 nm as characteristic of this species. It was also shown that the value of the rate constant for the disproportionation at zero U(VI) concentration did not obey a strictly first-order acid dependency but tended to be slightly lower than expected as the acid concentration was increased.

The present study was undertaken to extend the work of Newton and Baker to higher acid concentrations, to measure the absorption spectra of U(V) and of the $U^V \cdot U^{VI}$ complex in the visible region, to reexamine the effect of deuterium substitution on the rates of disproportionation of U(V), and to determine the effect of selected anions on the reaction rate.

Experimental Section

Reagents. Solutions of $UO_2(ClO_4)_2$, $HClO_4$, $NaClO_4$, $Eu(ClO_4)_3$, and the equivalent solutions in D_2O were prepared and analyzed as described previously.[3,4] $Mg(ClO_4)_2$, which was added to the reagents in concentrations such that the sum of the UO_2^{2+} and Mg^{2+} concentration remained constant,[2] was obtained by twice recrystallizing a commercial product (Merck), the stock solution of the product being

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(1) (a) D. M. H. Kern and E. F. Orlemann, *J. Amer. Chem. Soc.*, 71, 2102 (1949); (b) E. F. Orlemann and D. M. H. Kern, *ibid.*, 75, 3059 (1953); (c) K. A. Kraus, F. Nelson, and G. L. Johnson, *ibid.*, 71, 2510 (1940); (d) F. R. Duke and R. C. Pinkerton, *ibid.*, 73, 2361 (1951); (e) J. Koryta and J. Kouteky, *Collect. Czech. Chem. Commun.*, 20, 423 (1955); (f) H. Imai, *Bull. Chem. Soc. Jap.*, 30, 873 (1957).

(2) T. W. Newton and F. B. Baker, *Inorg. Chem.*, 4, 1166 (1965).

(3) A. Ekstrom and Y. Farrar, *Inorg. Chem.*, 11, 2610 (1972).

(4) A. Ekstrom and D. A. Johnson, *J. Inorg. Nucl. Chem.*, in press.

analyzed by EDTA titration.[5] Eu(II) solutions containing the appropriate quantities of $NaClO_4$ and $HClO_4$ were prepared by electrochemical reduction of Eu(III) at a mercury cathode in a thermostated cell described elsewhere.[3] All solutions were carefully purged with argon gas from which residual traces of oxygen were removed by passage of the gas through a column of the appropriate activated catalyst (BASF catalyst No. R3-11).

Procedure. The reactions were measured using a stopped-flow apparatus and the computerized data aquisition system already described.[6] The primary data (reagent concentrations and the transmittance *vs.* time readings) were acquired in the form of punched tape, this being virtually essential in view of the very large number of runs required for this investigation.

The U(V) was prepared *in situ* by allowing Eu(II) to react with U(VI) in the stopped-flow apparatus. Previous work[4] had shown that the Eu(II)-U(VI) reaction is very rapid ($k = 1.4 \times 10^4\ M^{-1}\ \text{sec}^{-1}$ at $I = 2.0$, 20°), while the reaction of Eu(II) with U(V) is very slow. The U(VI) concentrations were varied by treating a constant quantity of Eu(II) with increasing amounts of U(VI). Each rate constant was determined by averaging the results of four to eight measurements. The value of the disporportionation rate constant at zero U(VI) concentration for a given set of experimental parameters was determined, as will be described in detail below, by extrapolating the values determined at ten different U(VI) concentrations.

The reactions were usually followed by measuring the rate of appearance of U(IV) at 640 nm and analyzed according to a second-order rate law

$$d[U(IV)]/dt = -2d[U(V)]/dt = k_2[U(V)]^2 \qquad (2)$$

Since the extinction coefficient of U(VI) is negligible at 640 nm, it follows from the stoichiometry of eq 1 that at the completion of the reaction the extinction coefficient of U(IV) is given for a 1-cm path length cell by the expression

$$\text{EU4} = \text{ABSF}[0.5A_0]^{-1} \qquad (3)$$

where ABSF is the absorbance of the reacting solution at $t = \infty$ and A_0 is the initial U(V) concentration. The constancy of the calculated value of EU4 can thus be used to estimate the completeness of the deoxygenation of the solutions and of the reduction of the Eu(III) solutions.

Least-squares analyses were carried out using a program described by Lietzke,[7] the data being weighted according to the reciprocal of the square of the per cent mean deviation.

Results

Excellent straight lines up to 90% reaction were obtained when the experimental results were plotted according to a second order rate law. In agreement with a previous study,[2] it was observed that the rate constant for the reaction decreases noticeably with increasing U(VI) concentration (Table I). This effect has been attributed[2] to the formation of a $U^V \cdot U^{VI}$ binuclear complex (eq 4-6), and on the basis of

$$U(V) + U(VI) \overset{K_e}{\rightleftharpoons} U^V \cdot U^{VI} \qquad (4)$$

$$2U(V) \xrightarrow{k_5} U(IV) + U(VI) \qquad (5)$$

$$U^V \cdot U^{VI} + U(V) \xrightarrow{k_6} U(IV) + 2U(VI) \qquad (6)$$

this reaction sequence, it can be readily shown that

$$k_2(\text{obsd}) = \{k_5 + k_6K_e[U(VI)]\}\{1 + K_e[U(VI)]\}^{-2} \qquad (7)$$

Least-squares analysis of the data in terms of eq 7 leads to values of K_e and k_5 in good agreement with those reported previously,[2] while in our study the value of k_6 in this and subsequent runs was invariably found to be slightly negative or zero within the experimental error. Because U(VI) ions are formed in the course of the disproportionation reaction, the U(VI) concentration was taken as equal to that at 50% reaction, *i.e.*, $[U(VI)] = [U(VI)]_0 + 0.25[U(V)]$. The choice of this value for the U(VI) concentration is somewhat arbitrary, but the values of k_5 and K_e calculated according to eq 7 were found not to be particularly sensitive to small changes in the U(VI) concentration. Thus if [U(VI)] was taken as $[U(VI)]_0$, the values of k_5 and K_e for the above run (Table I) were calculated as $(3.47 \pm 0.08) \times 10^2\ M^{-1}\ \text{sec}^{-1}$ and $13.9 \pm 0.6\ M^{-1}$, respectively.

Table I. Effect of U(VI) Concentration on the Rate Constant for the Disproportionation of U(V)[a]

$10^2[U(VI)]$, M	EU4,[b,c] $cm^{-1}\ M^{-1}$	$10^{-2}k_2, M^{-1}\ sec^{-1}$		
		Obsd[c]	Calcd[d]	Calcd[e]
0.996	39.6 ± 0.9	2.79 ± 0.04	2.82	2.80
1.48	40.5 ± 0.1	2.60 ± 0.06	2.52	2.53
1.97	40.6 ± 0.2	2.72 ± 0.05	2.26	2.28
2.46	40.3 ± 0.3	2.07 ± 0.03	2.05	2.07
2.59	40.7 ± 0.3	1.87 ± 0.03	1.87	1.88
3.44	40.6 ± 0.2	1.71 ± 0.05	1.70	1.70
3.94	40.6 ± 0.2	1.59 ± 0.04	1.56	1.55
4.42	39.2 ± 0.9	1.34 ± 0.06	1.43	1.41
4.92	40.4 ± 0.3	1.31 ± 0.03	1.32	1.29
5.41	39.7 ± 0.8	1.18 ± 0.04	1.23	1.17

[a] $[U(V)]_0 = 1.30 \times 10^{-2}\ M$, $[H^+] = 0.75\ M$, ionic strength 2.50, 20°; reaction measured at 640 nm. [b] Extinction coefficient of U(IV). [c] Errors quoted are mean deviations for six to eight runs at each U(VI) concentration. [d] Calculated from eq 7 with $k_5 = (3.61 \pm 0.05) \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $k_6 = 0.0$, and $K_e = 13.2 \pm 0.4\ M^{-1}$. [e] Calculated from eq 7 with $k_5 = (3.48 \pm 0.07) \times 10^2\ M^{-1}\ \text{sec}^{-1}$, $k_6 = (-1.92 \pm 1.09) \times 10^2\ M^{-1}\ \text{sec}^{-1}$, and $K_e = 8.84 \pm 1.80\ M^{-1}$.

The acid concentration dependency of the rate constant was studied in the range 0.25-2.00 M H^+ at an ionic strength of 2.50 and 20°. At each acid concentration the rate constant was determined at ten different U(VI) concentrations and the values of k_5 (the rate constant at zero U(VI) concentration) and the equilibrium constant K_e were determined by least-squares analysis of the data in terms of eq 7. The results obtained (Table II) show that, as expected, the value of k_5 increased with increasing acid concentration although as indicated by the lack of constancy of the term $k_5[H^+]^{-1}$, the dependency of k_5 on the acid concentration is not, as observed previously,[2] strictly first order. The results also show that the value of K_e is independent of acid concentration, the average for all values being $13.8 \pm 1.2\ M^{-1}$.

The effects of acid concentration on the values of k_5 and K_e were also measured in fully deuterated solutions. As mentioned above, Duke and Pinkerton[1d] had observed that contrary to common experience,[8] the rate of disproportionation was faster in D_2O than in H_2O. It was originally thought that deuterium substitution might decrease the value of K_e, thereby indirectly increasing the value of the observed rate constant. However, as shown by the results summarized in Table III the values of both k_5 and K_e were found to be measurably higher in D_2O than in H_2O at all concentrations. Thus the ratio of $K_e^{D_2O}/K_e^{H_2O}$ was determined at 1.27 while an average value of 1.29 was obtained for the ratio $k_5^{D_2O}/k_5^{H_2O}$ at the various acid concentrations. It may also be noted that the value of k_5 again does not obey a strictly first-order acid dependency.

The absorption spectra of U(V) and of the $U^V \cdot U^{VI}$ complex were measured at 20-nm intervals for a solution containing 0.25 M H^+, at an ionic strength of 2.50 and at 20°.

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(5) F. J. Welcher, "Analytical Uses of Ethylenediamine Tetraacetic Acid," Van Nostrand, Princeton, N. J., 1958.

(6) A. Ekstrom, *Inorg. Chem.*, 12, 2455 (1973).

(7) M. H. Lietzke, U. S. Atomic Energy Commission Report No. ORNL 3259, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(8) The rates of electron-transfer reactions are usually observed to be slower in D_2O than in H_2O. See for example J. Hudis and R. W. Dodson, *J. Amer. Chem. Soc.*, 78, 912 (1956); see also ref 3 and 6.

Table II. Effect of Acid Concentration on the Values of K_e and k_5 in H_2O^a

$[H^+], M$	No. of determins^b	EU4, $cm^{-1} M^{-1}$	K_e,^{c} M^{-1}	$10^{-2}k_5$,^{c} M^{-1} sec^{-1} (obsd)	$10^{-2}k_5[H]^{-1}$, M^{-2} sec^{-1} (obsd)	Rms,^{d} %
2.00	67	40.5 ± 0.2	14.3 ± 0.07	7.96 ± 0.15	3.98	2.24
1.75	60	39.7 ± 0.5	13.0 ± 0.4	7.12 ± 0.10	4.06	2.01
1.50	61	39.8 ± 0.3	12.1 ± 0.7	6.74 ± 0.17	4.49	4.09
1.25	55	40.2 ± 0.4	13.6 ± 0.7	5.50 ± 0.18	4.40	2.69
1.00	61	40.5 ± 0.5	12.1 ± 0.4	4.55 ± 0.06	4.55	1.51
0.75	57	39.7 ± 0.2	13.2 ± 0.4	3.60 ± 0.05	4.80	2.84
0.50	55	39.3 ± 0.4	17.8 ± 0.6	2.91 ± 0.07	5.82	2.91
0.25	59	38.7 ± 0.3	14.0 ± 0.3	1.48 ± 0.02	5.92	1.65

[a] $[U(V)]_0 = 1.30 \times 10^{-2}$ M, ionic strength 2.50, 20°; reaction measured at 640 nm. [b] Reactions measured at ten U(VI) concentrations in the range 9.96×10^{-3}–5.41×10^{-2} M for each acid concentration. [c] Errors quoted are standard deviations. [d] Root-mean-square per cent deviation, given by $100[(1/n)\Sigma(k_{obsd} - k_{calcd})^2/k_{obsd}{}^2]^{1/2}$.

Table III. Effect of Acid Concentration on the Values of K_e and k_5 in D_2O^a

$[D^+], M$	No. of determins^b	EU4, $cm^{-1} M^{-1}$	K_e,^{c} M^{-1}	$10^{-2}k_5$,^{c} M^{-1} sec^{-1} (obsd)	$10^{-2}k_5[D^+]^{-1}$, M^{-1} sec^{-1}	Rms, %
0.25	52	39.8 ± 0.3	19.5 ± 0.8	1.85 ± 0.06	9.25	2.59
0.50	55	39.5 ± 0.5	17.8 ± 0.6	3.51 ± 0.07	7.02	2.67
0.75	55	40.1 ± 0.2	18.4 ± 0.4	4.78 ± 0.07	6.40	1.52
1.00	63	40.0 ± 0.3	15.6 ± 0.6	5.91 ± 0.12	5.91	3.06
1.25	61	39.8 ± 0.5	17.9 ± 0.2	7.62 ± 0.07	6.09	1.05
1.50	53	42.0 ± 0.4	15.7 ± 0.5	8.65 ± 0.24	5.77	2.51
1.75	56	41.2 ± 0.6	17.0 ± 0.5	9.62 ± 0.29	5.50	1.55

[a] $[U(V)]_0 = 1.20 \times 10^{-2}$ M, ionic strength 2.50, 20°; reaction measured at 640 nm. [b] Reactions measured at ten U(VI) concentrations in the range 1.34×10^{-2}–6.24×10^{-2} M for each acid concentration. [c] Errors quoted are standard deviations.

The U(V) spectrum was obtained by allowing 1.30×10^{-2} M Eu(II) to react with 1.35×10^{-2} M U(VI) since under these conditions practically none of the complex is formed. From measurements of the absorbance of the reacting solution at the completion of the U(VI)-Eu(II) reaction the extinction coefficients of U(V) may be readily evaluated. The spectrum of the $U^V \cdot U^{VI}$ complex was obtained in a similar manner except that in this case Eu(II) was treated with excess U(VI). The value of the equilibrium concentration of the complex (x_e) was evaluated from the expression

$$K_e = 13.8 = x_e\{[A_0 - x_e][B_0 - x_e]\}^{-1} \tag{8}$$

where A_0 and B_0 are respectively the initial concentrations of U(V) and U(VI). The extinction coefficient of the complex was then evaluated from

$$EC = \{ABSF - EU5[A_0 - x_e] - EU6[B_0 - x_e]\}x_e^{-1} \tag{9}$$

where ABSF is the absorbance of the solution a few milliseconds after the mixing of the reagents (see Figure 1) and EC, EU5, and EU6 are the extinction coefficients of $U^V \cdot U^{VI}$, U(V), and U(VI), respectively. The results obtained (Figure 2) show that the spectrum of U(V) is very weak but that a major absorption band may be located above 760 nm. In contrast, the spectrum of the complex shows two quite intense bands located at 400 and 740 nm. The extinction coefficient determined for the latter peak (EC 24.3 cm^{-1} M^{-1}) is in good agreement with the value of ~27 cm^{-1} M^{-1} determined by Newton and Baker[2] by a different method, thus confirming the validity of the procedure used in the present work.

The ionic strength dependency was determined by measuring k_5 and K_e in three sets of solutions ranging in ionic strength from 0.50 to 4.00 (Table IV). The results obtained clearly illustrate the marked ionic strength dependency of both k_5 and K_e, the value of k_5 increasing by nearly an order of magnitude when the ionic strength was increased from 0.50 to 4.00. Over the same range of ionic strength the value of K_e was found to increase from 5.1 ± 0.5 at $I = 0.50$ to 25.9 ± 0.2 at $I = 4.00$.

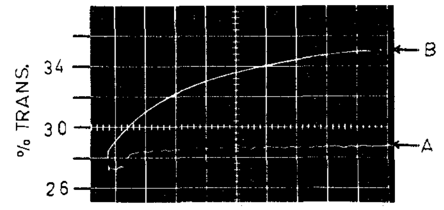

Figure 1. Illustration of the method used to determine the extinction coefficient of the $U^V \cdot U^{VI}$ complex, where $[U(V)]_0 = 1.30 \times 10^{-2}$ M, $[U(VI)] = 5.63 \times 10^{-2}$ M, $I = 2.50$, at 20° and 400 nm: trace A, 1.0×10^{-2} sec/major division, showing the formation of U(V) and $U^V \cdot U^{VI}$ from Eu(II) and U(VI); trace B, 1.0 sec/major division, showing the decomposition of U(V) and $U^V \cdot U^{VI}$.

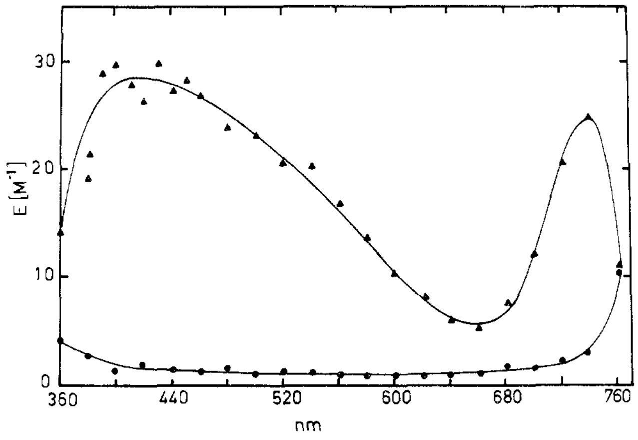

Figure 2. Absorption spectra of U(V) (●) and the $U^V \cdot U^{VI}$ complex (▲) obtained as described in text. $[U(V)] = 1.30 \times 10^{-2}$ M, $[H^+] = 0.25$ M, and $I = 2.50$, at 20°.

The addition of 5.63×10^{-3} M $SO_4{}^{2-}$ to the reacting solutions greatly increases the rate constant of the disproportionation reaction. Analysis of the data (Table V) in terms of eq 7 shows that the value of k_5 is increased from (1.48 ± 0.02) × 10^2 M^{-1} sec^{-1} in the absence of sulfate to (4.55 ± 0.09) × 10^2 M^{-1} sec^{-1}, while the value of K_e was increased from 14.0 ± 0.3 to 18.4 ± 0.6 M^{-1}. When the above run was repeated in the presence of 2.82×10^{-2} M $SO_4{}^{2-}$, the

Table IV. Effect of Ionic Strength on the Values of K_e and k_5[a]

Ionic strength	No. of determins[b]	EU4,[c] cm^{-1} M^{-1}	$10^{-2}k_5$,[c] M^{-1} sec^{-1}	K_e,[c] M^{-1}
4.00	53	39.8 ± 0.4	4.08 ± 0.19	25.9 ± 0.2
2.50	59	38.7 ± 0.3	1.48 ± 0.02	14.0 ± 0.3
0.50	55	40.1 ± 0.5	0.43 ± 0.01	5.1 ± 0.5

[a] $[U(V)]_0 = 1.30 \times 10^{-2}$ *M*, $[H^+] = 0.25$ *M*, 20°; reaction followed at 640 nm. [b] Measured at ten different U(VI) concentrations in the range 9.92×10^{-3}–5.41×10^{-2} *M*. [c] Errors quoted are standard deviations.

Table V. Effect of Sulfate and Chloride Concentration on the Values of K_e and k_5[a]

Anion	No. of determins[b]	K_e,[c] M^{-1}	$10^{-2}k_5$,[c] M^{-1} sec^{-1}
5.63×10^{-3} *M* SO_4^{2-}	67	18.4 ± 0.6	4.55 ± 0.09
2.82×10^{-2} *M* SO_4^{2-}	69	~38	~20
2.50 *M* Cl^-	62	8.1 ± 0.4	2.99 ± 0.05

[a] $[U(V)]_0 = 1.30 \times 10^{-2}$ *M*, $[H^+] = 0.25$ *M*, $I = 2.50$, 20°; reaction measured at 640 nm. [b] Reaction measured at ten U(VI) concentrations over the range $(1.17–5.49) \times 10^{-2}$ *M*. [c] Values calculated according to eq 7; errors quoted are standard deviations.

rate of reaction was found to be very rapid ($k_5 \approx 2 \times 10^3$ M^{-1} sec^{-1}), and the value of K_e was determined as ~38 M^{-1}. For these experiments it was found that the plots of the integrated rate equation were no longer straight lines, indicating that a simple second-order rate law was no longer applicable.

A similar, although more pronounced effect was noted when 5.00×10^{-3} *M* F^- ion was added to the reactant solution. For these runs the plots of the integrated rate equation were so strongly curved as to preclude the determination of meaningful rate constants.

The addition of small (<0.1 *M*) concentrations of Cl^- ion was found to result in only a marginal effect on the values of k_5 and K_e, but in a pure chloride medium ($[Cl^-] = 2.50$ *M*, $[H^+] = 0.25$ *M*, $I = 2.50$) the value of k_5 was found to be approximately twice that measured for a perchlorate solution of similar acidity and ionic strength, while the value of K_e was observed to be decreased to 8.1 ± 0.4 M^{-1}.

An unusual effect was observed when Eu(II) was treated with U(VI) at low acidities. When 1.30×10^{-2} *M* Eu(II) was mixed with an equal concentration of U(VI), a simple reaction trace resulted showing (Figure 3, upper photograph) the rapid formation of U(V) followed by the slow disproportionation of the U(V) indicated by the decrease in the per cent transmission due to the formation of U(VI). In the presence of a small excess (0.75×10^{-2} *M*) of U(VI) the reaction traces (Figure 3, lower photograph) again showed the very rapid formation of U(V) but on a slow time scale the reaction trace clearly showed an initial increase in absorbance, followed by a slower decrease. This effect, which could be observed only over a very narrow range ($(0.7–0.9) \times 10^{-2}$ *M*) of U(VI) concentrations indicates that under these conditions at least two simultaneous reactions are occurring, one of which is presumably the disproportionation of U(V). Unfortunately the combination of the small absorbance changes and relatively rapid reaction rates precluded a more detailed study of this observation.

Discussion

The present results are consistent with the previous observation[2] that the rate constant for the disproportionation reaction does not follow a strictly first-order acid dependency. Several possible causes of this deviation may be considered,

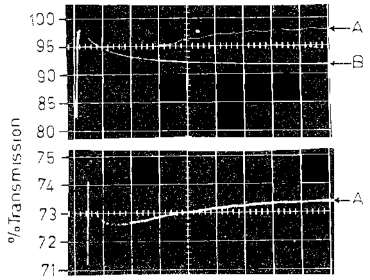

Figure 3. Upper photograph: reaction traces obtained when no excess U(VI) was present in the reactant solutions: trace A, 1×10^{-2} sec/division showing the formation of U(V); trace B, 1 sec/division, illustrating the disproportionation of U(V). Lower photograph: reaction trace obtained in the presence of 0.75×10^{-2} *M* excess U(VI), 2 sec/division. $[U(V)]_0 = 1.30 \times 10^{-2}$ *M*, $[H^+] = 0.10$ *M*, and $I = 2.50$, at 20° and 410 nm.

the first being a medium effect, represented by the expression

$$k_2(\text{obsd}) = k_0[H] \exp\{\alpha[H]\}\{1 + K_e[U(VI)]\}^2 \qquad (10)$$

In the present work no systematic variation in K_e with acid concentration was observed, so that the Harned correction[9] was applied only to the value of k_5. The above expression is able to reproduce the experimental data quite well (Table VI) but requires the value of the Harned parameter α to be negative in both H_2O and D_2O. Although the prediction of the sign and value of α for these reactions is difficult, past work[10] has usually shown α to be positive for reactions between cations.

An alternative interpretation of the present results can be made in terms of eq 11 which can be readily obtained from

$$k_2(\text{obsd}) = k_0K[H]\{[1 + K[H]]^2[1 + K_e[U(VI)]]^2\}^{-2} \qquad (11)$$

the reaction sequence

$$UO_2^+ + H^+ \overset{K}{\rightleftharpoons} UO_2H^{2+} \qquad (12)$$

$$UO_2H^{2+} + UO_2^+ \xrightarrow{k_0} \text{products} \qquad (13)$$

in combination with eq 4 and 5. Equation 11 will give a first-order acid dependency only if $K[H] << 1$ so that in this mechanism the deviation from a first-order dependency is attributed to the presence of significant concentrations of the UO_2H^{2+} complex. The formations of this[1a] and the analogous NpO_2H^{2+} [11] species have been suggested on several occasions, but apart from inconclusive spectroscopic evidence for the NpO_2H^{2+} complex,[12] no convincing evidence for the presence of these species has been obtained. Analysis of the present results in terms of eq 11 leads to values of *K* which are not unreasonable (Table VI) but requires an isotope effect ($K_{H_2O}/K_{D_2O} = 1.78$) which seems large for these strongly acidic complexes.[13]

The value of this isotope effect is reduced to 1.49 when a

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(10) (a) T. W. Newton, *J. Phys. Chem.*, 74, 1655 (1970); (b) T. W. Newton and N. A. Daugherty, *ibid.*, 71, 3768 (1967); see also ref 4 and 6.

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(12) R. Sjoblom and J. C. Hindman, *J. Amer. Chem. Soc.*, 73, 1744 (1951); see also ref 11.

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Table VI. Summary of the Values of the Parameters Determined by Least-Squares Analysis

Medium	Eq. no.	k_0[b]	K_e[b]	K[b]	α[b]	Rms, %
H_2O (80 data points)	10	$(5.52 \pm 0.14) \times 10^2$	13.4 ± 0.4		−0.17 ± 0.01	5.92
	11	$(5.81 \pm 0.31) \times 10^3$	13.4 ± 0.4	$(9.58 \pm 0.7) \times 10^{-2}$		5.85
	14	$(3.45 \pm 0.10) \times 10^3$	13.3 ± 0.4	$(1.64 \pm 0.08) \times 10^{-1}$	0.10[a]	5.77
	17	$(3.88 \pm 0.24) \times 10^{-4}$	13.3 ± 0.4	$(1.77 \pm 0.05) \times 10^{-3}$		5.79
D_2O (70 data points)	10	$(6.88 \pm 0.13) \times 10^2$	17.4 ± 0.3		−0.10 ± 0.02	4.95
	11	$(1.27 \pm 0.18) \times 10^4$	17.4 ± 0.3	$(5.44 \pm 0.09) \times 10^{-2}$		4.94
	14	$(6.11 \pm 0.43) \times 10^3$	17.4 ± 0.3	$(1.14 \pm 0.10) \times 10^{-1}$	0.10[a]	4.94
	17	$(1.67 \pm 0.26) \times 10^{-4}$	17.4 ± 0.3	$(1.44 \pm 0.29) \times 10^{-3}$		4.94

[a] The value of this parameter was fixed. [b] Errors are standard deviations.

Harned correction is applied to the value of k_0 in eq 11 to yield the expression

$$k_2(\mathrm{obsd}) = k_0 \{\exp \alpha[\mathrm{H}]\}K[\mathrm{H}]\{[1 + K[\mathrm{H}]]^2 [1 + K_e[\mathrm{U(VI)}]]^2\}^{-1} \tag{14}$$

For this analysis, the value of the Harned parameter was set equal to +0.10 which is representative of the values usually found for reactions between cations. In a previous study of the effect of deuterium substitution,[1b] it was suggested that the reaction rate was enhanced in D_2O compared to H_2O because the value of K was larger in the former solvent. The present results indicate that if the results are interpreted in terms of eq 11 or 14, this interpretation is incorrect and that the increase in the reaction rate is due entirely to an increase in the value of k_0 in eq 12.

The experimental results were also tested for the reaction sequence

$$2\mathrm{U(V)} \overset{k_{15}}{\rightleftharpoons} [\mathrm{U(V)}]_2 \tag{15}$$

$$[\mathrm{U(V)}]_2 + \mathrm{H}^+ \xrightarrow{k_{16}} \text{products} \tag{16}$$

which on application of the steady-state approximation to the U(V) dimer concentration leads to the expression

$$k_2(\mathrm{obsd}) = [\mathrm{H}]\{K + k_0[\mathrm{H}]\}^{-1}\{1 + K_e[\mathrm{U(VI)}]\}^{-2} \tag{17}$$

where $K = k_{-15}[k_{15}k_{16}]^{-1}$ and $k_0 = k_{15}$. As shown in Table VI, this model also fits the experimental results and yields a value for the rate constant for the formation of the U(V) dimer which is greater in D_2O than in H_2O, the ratio of the two rate constants being 2.32.

It is clearly not possible to express a preference for any of the above three reaction mechanisms solely on the basis of the fit of the experimental data to the various models, but it is interesting to note that deuterium substitution increases the value of K_e and k_5 by nearly the same ratio. This observation suggests a similar role of water molecules in the formation of the $\mathrm{U^V{\cdot}U^{VI}}$ complex and the transition complex and might be cited as evidence for a disproportionation mechanism involving a U(V) dimer. As indicated previously,[2] this mechanism is further supported by the relatively high values found for the equilibrium constant of the $\mathrm{U^V{\cdot}U^{VI}}$ complex and by the observation in the present study that the rate of formation of the U(V) dimer would be higher in D_2O compared to H_2O. The precise role of the H_2O or D_2O molecules in the mechanism of the formation of the $\mathrm{U^V{\cdot}U^{VI}}$ complex and U(V) dimer is difficult to evaluate at this time but the unusual isotope effect may be the result of changes in the degree of metal ion hydration in the two solvents[14] as well as variations in the rates of replacement of coordinated water molecules.

The values of K_e and k_5 were both increased by the addition of small concentrations of SO_4^{2-} but k_5 was only slightly increased and K_e slightly reduced in 2.5 M Cl^- ion. The effect of Cl^- ion on the value of K_e is similar to that observed for the $\mathrm{Np^V{\cdot}U^{VI}}$ complex[15] and may reflect a change in the appropriate activity coefficients, but the effect of SO_4^{2-} suggests that this ion may act as a bridging anion in this system. Similarly, the strong ionic strength dependency of both constants may be a reflection on the participation of the ClO_4^- ion in the formation of the $\mathrm{U^V{\cdot}U^{VI}}$ complex and of the transition-state complex.

A previous study[6] has revealed major differences in both the rate constants and rate parameters for the decomposition of the $\mathrm{U^V{\cdot}Cr^{III}}$ and $\mathrm{Np^V{\cdot}Cr^{III}}$ complexes, and it was suggested that the effect may be indicative of the participation of the 5f orbitals in bonding in these species. The marked difference in the equilibrium constant for the $\mathrm{U^V{\cdot}U^{VI}}$ complex ($K_e = 13.4$ at 20°, $I = 2.50$) and the equivalent $\mathrm{Np^V{\cdot}U^{VI}}$ complex ($K_e = 0.69$ at 25°, $I = 3.00$)[15] may similarly be a reflection on the differences in the bonding resulting from the replacement of a U(V) ($5f^1$) ion by a Np(V) ($5f^2$) ion.

Previous determinations of the absorption spectrum of U(V) ions[16] have revealed some absorption bands in the near-infrared region and a featureless absorption which increases quite sharply with decreasing wavelength below approximately 500 nm. In the present work, no evidence for this latter absorption was found in the spectrum of the U(V) ion. A possible interpretation of this discrepancy is that the solutions used in earlier attempts to measure the U(V) spectra contained substantial concentrations of U(VI) and hence of the $\mathrm{U^V{\cdot}U^{VI}}$ complex which the present study has shown to have quite intense absorption in the region 400-600 nm.

The simplest interpretation of the results showing the occurrence of two relatively slow reactions at low U(VI) concentrations is that under these conditions part of the formation of the $\mathrm{U^V{\cdot}U^{VI}}$ complex, shown by the increase in absorbance, is observed. As the U(VI) concentration is increased, the rate of this reaction presumably becomes comparable to that of the Eu(II)-U(VI) reaction so that no indications of the former can be observed. The results of a simulation of this situation by Runge-Kutta calculations[6] yielded qualitative agreement with the experimental observation, but, as indicated above, it was found impossible to examine the effect in greater detail.

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Registry No. U(VI), 22541-40-8; U(V), 22537-60-6.

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(14) It is of interest to note that deuteration frequently increases the length of hydrogen bonds, at least in the solid state (see, *e.g.*, R. G. Delaplane and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 2423 (1969)). If the formation of the $\mathrm{U^V{\cdot}U^{VI}}$ complex involved hydrogen bonding, the interuranium distances of the complex in D_2O might be longer than in H_2O, resulting in a decrease in the electrostatic repulsion between the positive ions.

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