creasing μ. This effect tends to cause k_1 to decrease as μ increases but in these experiments is so small as to require only a slightly greater variation in the activity coefficient ratios than mentioned under discussion of the dissociation mechanism.

We conclude therefore that no evidence for the anion term in the rate law exists and that the simpler representation is the most likely one. This conclusion is further supported by the observations that the rate is not greatly affected by the identity of the ions at a given ionic strength. In addition, one can extrapolate k_1 values for NO_3^- and ClO_4^- systems to $\mu = 0$ obtaining the values of k_1 at 27° of $2.15 \pm 0.15 \times 10^4$ min.$^{-1}$ and $2.00 \pm 0.10 \times 10^{-4}$ min.$^{-1}$, respectively, essentially identical as the k_1 law predicts.

The last experiment in Table I in which 3.34 *M* $(C_2H_5)_4NBr$ was present is interesting in that it represents the only known case in which the rate of exchange of water is not increased, and probably decreased by added salt. NaBr for example speeds up the exchange.[2] No explanation is possible at this time.

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Photostationary State Kinetics[1]

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Photoactivated uranyl ions reacting in water with methanol have been discovered to produce an intermediate U(V) species whose disproportionation into U(IV) and U(VI) gives rise to an after effect from which the concentration and rate of decay of the intermediate species has been determined. The steady state concentration of the intermediate species and the build-up to the steady state value have been measured as a function of the duration and extent of the photochemical reaction, the light intensity and the temperature. The results confirm the theory of the steady state. The thermal disproportionation of the U(V) has been found to have an activation energy of 17.3 kcal. in perchlorate solution at *p*H 1 and an ionic strength of unity. The entropy of formation of the critical complex in the same solution at 25° is +8.3 e.u. and ΔF^* equals 14.2 kcal.

Introduction

In most reactions involving intermediate species it is possible to measure only the rate of the overall reaction and then it is usually assumed that the concentrations of the intermediate species are at steady state values which are obtained by equating the rate of formation of every intermediate to its rate of decay. This procedure is justified when it provides a satisfactory quantitative interpretation of the kinetics of the reaction although actually the steady state is never quite attained. Sometimes, however, the intermediate species can be produced by light and it then becomes possible to measure also the rate of initiation of the reaction and the average life time of the intermediate species by employing intermittent illumination. When this is done, it has been shown[2] that the steady state theory permits a complete solution of the kinetics of the reaction.

We have been able to test the theory of the steady state more directly and exhaustively than heretofore by means of the photochemical reaction in water between methanol and photoactivated uranyl ions. We have discovered that this reaction produces an intermediate U(V) species whose concentration we have been able to measure both at steady state values and at values less than these as a function of the rates of formation and decay of this species. These rate changes have been produced by changes in the light intensity, temperature, and duration and extent of the reaction.

The discovery of U(V) as an intermediate in reactions of this kind, although not in this particular reaction, was made some time ago in this Laboratory[3] but the influence of the light intensity, temperature, and extent of the photochemical reaction upon the concentration of this species and the relation of this concentration to the steady state value has not been demonstrated previously.

The concentration of the U(V) has been evaluated from the after effect produced by the disproportionation of the U(V) into U(IV) and U(VI) which persists for several minutes immediately following photolysis as revealed by a transient increase in the optical density of the solution especially at the light absorption peak of U(IV) near 6500 Å. The measurements were found to eliminate the need for employing intermittent actinic illumination as a measuring device and for employing only weakly absorbed actinic light provided the solutions were stirred adequately.

The formulas of the unhydrolyzed U(IV), U(V) and U(VI) species are believed[4] to be $U(H_2O)_8^{+4}$, $UO_2(H_2O)_6^{+1}$ and $UO_2(H_2O)_6^{+2}$, respectively.

Experimental

Initial concentrations of the uranyl perchlorate and methanol in most expts. were 0.01 and 0.2 mole per liter, respectively. The concentration of perchloric acid was adjusted from 0.5 *M* to a *p*H of 1.03 ± 0.02 by adding sodium bicarbonate. The ionic strength was adjusted to unity by means of sodium perchlorate.

The stock solution of uranyl perchlorate was prepared in

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(1) Appreciation is expressed to Miss Elaine E. Geddes, B.A. (1953), Emmanuel College, Boston, Mass., for aid in the experimental part of the work and to the Charles F. Kettering Foundation and the Godfrey L. Cabot Fund of M.I.T. for financial support. This is publication No. 54 of the M.I.T. Solar Energy Conversion Project.

(2) A comprehensive and critical review of the theory regarding the concentration of active intermediates has been published by G. M. Burnett and H. W. Melville, "Technique of Organic Chemistry," S. L. Friess and A. Weisberger, Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, pp. 133–158.

(3) L. J. Heidt and K. A. Moon, THIS JOURNAL, **75**, 5803 (1953).

(4) (a) K. A. Kraus, F. Nelson and G. L. Johnson, *ibid.*, **71**, 2510 (1949); (b) K. A. Kraus and F. Nelson, *ibid.*, **71**, 2517 (1949); (c) *ibid.*, **72**, 3901 (1950). The uranous species, however, may well be $U(H_2O)_6^{+4}$ instead of $U(H_2O)_8^{+4}$. See also J. Sutton, *Nature*, **169**, 235 (1952).

the manner previously described.[3] All other chemicals were of the best commercial grade.

The apparatus employed to irradiate the solutions and the actinometry have been described.[5] The volume of the irradiated solution was 32 ml. in every case. The actinic light was more than 98% of 2537 Å.; it was filtered free of all wave lengths shorter than 2537 Å. and of most longer wave lengths in the manner previously described.[5]

Optical densities, $D = \log_{10}(I_0/I)$, were measured with a Cary recording spectrophotometer. The optical density and wave length scales of the instrument had been calibrated in the manner previously described.[6] The cell compartment of the Cary was thermostated within 0.1° of the water-bath in which the solutions were photolyzed.

Absorbance values, A, attributable to light absorbed by solute species equal $(D_p - D_a) - (D_n - D_a) = D_p - D_n$ when D_a remained constant as was usually the case. D_p, D_n and D_a are the recorded values of the optical density when there was only air in the lower compartment of the Cary and when the beam of light in the upper compartment passed through the absorption cell containing a depth of ten cm. of the photolyzed solution in the case of D_p and of the unphotolyzed solution in the case of D_n and when the beam passed only through air in the case of D_a. The change in the value of D_p with time for a given solution equaled the change in A when other variables remained unchanged as in the case of the observed transient increase of D in the photolyzed solutions.

The *p*H measurements were made at room temperatures of 24 ± 1° with a Cambridge Instrument Co. Model R. *p*H Meter using their external glass electrode assembly in the recommended way.

Concentrations of U(IV) were obtained chemically and spectrophotometrically. They were determined chemically from the amount of iodine required to oxidize the U(IV) to U(VI) after the solutions had been brought to room temperature and had been buffered with a solution of a mixture of sodium carbonate and bicarbonate at *p*H 9.5. The amount of iodine consumed was determined after the reaction with iodine had been allowed to proceed for 4, 8 and 12 minutes. Reaction with iodine was stopped by acidifying the solution with sulfuric acid whereupon the excess iodine was titrated with thiosulfate. In every case plots of the iodine consumed against the duration of the reaction in alkaline solution fell, within the limits of error, on straight lines whose values at zero time gave the amount of U(IV) oxidized by the iodine. The method was developed in this Laboratory by Dr. and Mrs. Kenneth A. Moon.

The U(IV) concentrations were determined spectrophotometrically from the absorbance of the U(IV) species at the peak near 6500 Å. The absorbance at this peak has been found[4] to decrease with increase in *p*H especially above *p*H 1.3, but over the narrow *p*H range of 1.00 to 1.10 covered in our expts. the value of the absorption coefficient, ϵ_4, of the U(IV) per gram atom per liter per cm. was observed to be between 53 and 47 at 10 to 40°. The decrease in ϵ_4 with increasing *p*H has been attributed[4] to hydrolysis of U^{+4} and to dimerization of the hydrolyzed species after the manner that had been previously shown to take place in the case of ceric species.[7] The U(V) and U(VI) do not absorb light in this region of the spectrum.[4] The concentration of the U(IV) in moles per liter, therefore, equals, in our solutions, $A/10(50) = 0.002A$ where A is the absorbance of the solute species in the solution at the U(IV) peak near 6500 Å. per ten cm. depth of the solution and $\epsilon_4 = 50$.

Results and Discussion

Part I. Relative Quantum Yields.—Quantum yields, ϕ, for the production of U(IV) by light of 2537 Å. were found not to depend strongly upon the concentration of the uranyl ion, the light intensity, the temperature or the extent of the reaction within reasonable limits. This is shown in Fig. 1 where it will be seen that there is no consistent trend in ϕ with changes in any of these variables. Over 95% of the light of 2537 Å. was absorbed by the U(VI) and ϕ was of the order of tenths.

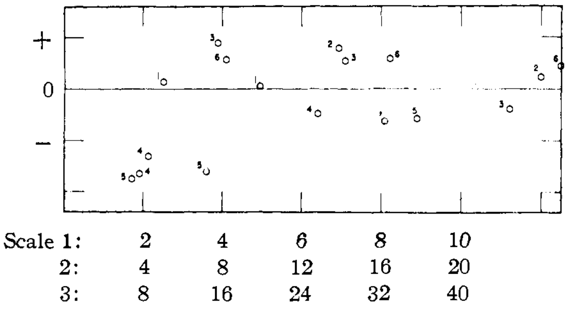

Fig. 1.—Deviations of quantum yields, ϕ, from the mean value, $\Sigma\phi F/\Sigma F$, plotted against F, the per cent. U(VI) eventually reduced to U(IV). ϕ equals moles U(VI) converted to U(IV) per mole of light quanta of 2537 Å. absorbed by the U(VI) in the system. The initial concentration of the methanol was 0.2 M in these expts. Points labeled 4 are for a solution initially 0.002 M in uranyl perchlorate compared to 0.01 M in all other expts. The light intensities, I, tabulated below are relative values. There appears to be no systematic trend in ϕ with changes in the extent of the reaction, the light intensity, the temperature and the initial concentration of the U(VI) under the conditions employed. The deviations in ϕ can be attributed to uncertainties in the chemical method of analysis for the U(IV).

Points	Temp., °C.	I	Scale of F
1	14	7.6	1
2	14	7.6	3
3	14	28	1
4	25	24	2
5	28	19	2
6	35	30	1

It was found that the absorption coefficient of the U(VI) species for light of 2537 Å. was about 500 per gram atom of U(VI) per liter per cm. in these solutions and to be unaffected by the methanol and sodium perchlorate, neither of which absorbed a measurable fraction of this light.

It was also found that an increase of about tenfold in the usual rate of stirring had no measurable effect upon ϕ. The usual rate of stirring swept the walls clean about ten times every second. In the case of solutions 0.01 M in uranyl perchlorate, the one-mm. layer of solution next to the wall of the reaction vessel absorbed about 70% of the light of 2537 Å. and contained about 7% of the solution. The duration of the average photolysis was about 150 seconds, hence less than $(0.1/150)70 = 0.05\%$ of the total reaction took place in this one-mm. layer between sweeps of the stirrer and there was always a great deal less than 0.05/0.07 or 0.7% difference between the concentrations of the products in this zone and their gross concentrations because of the turbulence of the solution between sweeps. Whereas if the solution had not been stirred and diffusion had been negligible, the concentrations of

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[5] L. J. Heidt and A. F. McMillan, This Journal, **76**, 2135 (1954).

[6] L. J. Heidt and D. E. Bosley, *J. Opt. Soc. Am.*, **43**, 760 (1953).

[7] L. J. Heidt and M. E. Smith, This Journal, **70**, 2476 (1948). The existence of ceric dimers has been questioned by M. G. Evans and N. Uri, Soc. Expt. Biol. Symposia, No. V, "Photosynthesis," Academic Press, Inc., New York, N. Y., 1951, p. 136, who have stated that "Our spectrophotometric measurements show conclusively that there is no dimerization." Their statement is remarkable in view of the fact that they present no definitive evidence in support of it. Later, spectrophotometric evidence in support of the existence of ceric dimers was obtained by T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951), and by E. L. King and M. L. Pandow, This Journal, **74**, 1966 (1952).

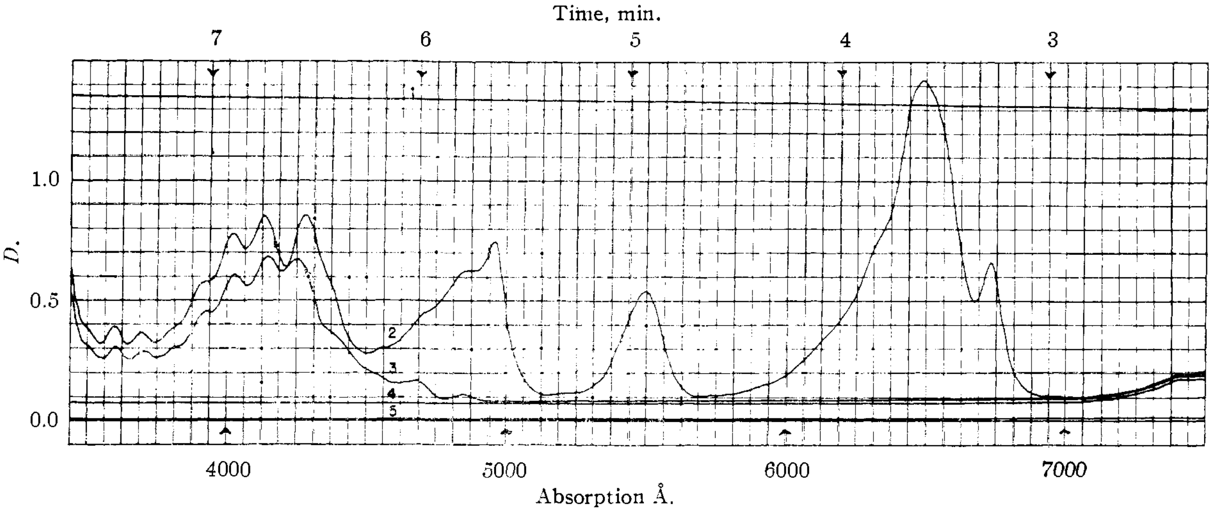

Fig. 2.—Absorption curves for photolyzed (curve 2) and unphotolyzed (curve 3) portions of a water solution of uranyl perchlorate and methanol at 14°, pH 1.03 and unit ionic strength. The photolysis was carried out with monochromatic light of 2537 Å. The absorption spectrum produced by the photolysis is the same as that of uranous ions.[3,4b] The decrease in D in the blue end of the spectrum is due to loss of uranyl, U(VI), ions eventually reduced to U(IV). Along the top of the Fig. the nearly horizontal line 1 depicts the observed transient increase in D with time at the strong U(IV) peak near 6500 Å. immediately after the photolysis had been terminated. Lines 4 and 5 depict the recorded values of the optical density of water in the same 10-cm. cell and of only air in the upper compartment of the Cary Spectrophotometer. There was only air in every case in the lower compartment of the Cary.

the products in this thin zone would have been as much as 1/0.07 or about 14 times their gross concentrations; such a situation and the accompanying depletion of the reactants in this zone would have interfered seriously with the interpretation of the results.

Part II. Evidence for the Photochemical Production of U(IV) and U(V).—The evidence for the production of U(IV) is illustrated by the absorption spectrum recorded in Fig. 2 for the products of the photolysis. This spectrum is identical in every respect with that of solutions of uranous perchlorate alone[4] or with methanol under about the same conditions.

The evidence for the U(V) species is illustrated partly by the slightly slanted line near the top of Fig. 2. This line portrays the transient increase with time in the optical density of the solution at the strong U(IV) peak near 6500 Å. immediately following photolysis. The difference between the final (primed) and the transient values of D, *i.e.*, $D' - D$, can be shown to be proportional to the concentration of the U(V) species. This is done by noting that in every case plots of $1/(D' - D)$ *vs.* time for the thermal reaction are linear when reasonable values are chosen for D'. The linearity of this relationship establishes the transient reaction as one of the second order with respect to the transient species. This is also the case when the transient species is produced by the illumination of solutions containing uranyl ions and carbohydrate material[3] instead of methanol and when U(V) thermally disproportionates into U(IV) and U(VI).[8] These facts and the pertinent information cited in the earlier work with carbohydrate material[3] leave little doubt that the transient species is indeed U(V).

Part III. Concentration of Intermediate U(V) Species and Kinetics of its Thermal Disproportionation into U(IV) and U(VI).—The concentration of U(V) in moles per liter equals $2(D' - D)/10(50) = 0.004(D' - D)$ where D' and D as mentioned in Part II represent the final and transient values, respectively, of the optical density produced by the transient after effect. The denominator, 10(50), contains the path length of 10 cm. of the light through the solution and the value of ϵ_4 which equals 50 in these solutions. The denominator, therefore, converts the difference $D' - D$ into moles of U(IV) per liter for reasons already stated and the factor 2 in the numerator is needed to convert the difference into moles of U(V) per liter since two moles of U(V) produces one mole of U-(IV).

The observed after-effects produced by the U(V) are plotted as filled and open circles in Figs. 3 and 4. The curved lines in these figures are based on reasonable values of D' and are seen to represent the data within the limits of error over most of the after-effect. The falling away of the points from the lines toward the end of the after-effect is attributable to thermal oxidation of a small amount of the U(IV) by the air. This oxidation was kept small during the spectrophotometric part of the work by stoppering every absorption cell after it had been completely filled with photolyzed solution.

The value of [U(V)] at the instant the photochemical reaction was terminated was obtained by extrapolating to zero time the linear plot of $1/(D' - D)$ *vs.* time. The value of D at zero time obtained in this way is designated D_0; hence $[\mathrm{U(V)}]_0 = 0.004(D' - D_0)$. The values of the slopes, S, of these plots are given in Table I.

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(8) (a) H. G. Heal and J. G. N. Thomas, *Trans. Faraday Soc.*, **45**, 11 (1949); (b) D. M. H. Kern and E. F. Orlemann, THIS JOURNAL, **71**, 2102 (1949); and (c) F. R. Duke and R. C. Pinkerton, *ibid.*, **73**, 2361 (1951).

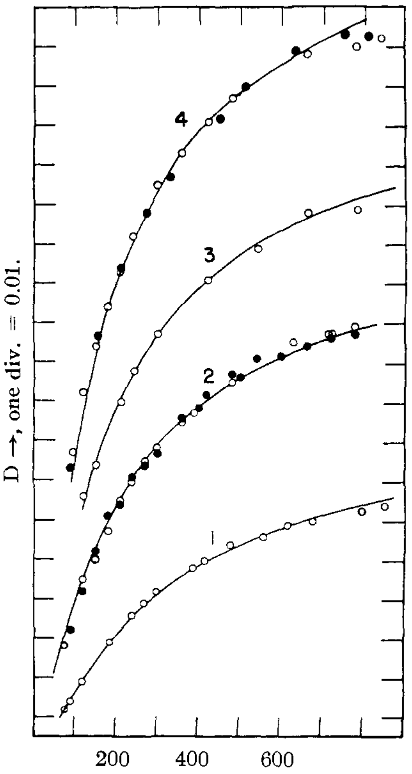

Fig. 3, Time, sec.

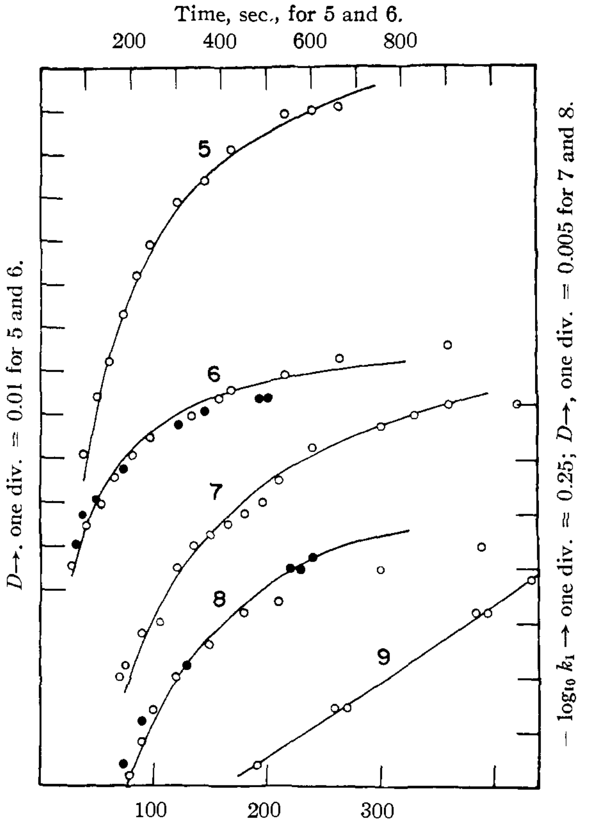

Fig. 4, Time, sec., for 7 and 8.

Figs. 3 (left) and 4 (right).—Experimental points and theoretical lines depicting the transient increase with time in optical density, D, at the absorption peak of U(IV) near 6500 Å. following the illumination with light of 2537 Å. of water solutions containing 0.01 M uranyl perchlorate, 0.2 M methanol and enough perchloric acid and sodium perchlorate to give a pH of 1.03 ± 0.02 and unit ionic strength. The values of D are for a ten-cm. depth of solution. The time scales in these Figs. represent seconds elapsed after the illumination with the actinic light had been discontinued. The plots are identified in Table I. Line 9 shows the linear dependence of the negative of the logarithm of the rate constant of the thermal disproportionation of the U(V) upon the reciprocal of the Kelvin temperature; the slope of line 9 gives an activation energy of 17.3 kcal. for the reaction. The mark on the abscissa nearest the lowest point on this line corresponds to a value of 325 for $10^5/T$ and one division on this scale equals ten of these units.

The rate constant k_1 for the thermal disproportionation of the U(V) into U(IV) and U(VI) is obtained[8] from the equation $-d[\mathrm{U(V)}]/dt = 2k_1 \cdot [\mathrm{H}^+][\mathrm{U(V)}]^2$; hence $2k_1[\mathrm{H}^+]t = 1/[\mathrm{U(V)}] = 1/0.004(D' - D)$ and $0.004[\mathrm{H}^+]2k_1 = 1/(D' - D)t$ which is the slope, S, of the plot of $1/(D' - D)$ *vs.* time. The value of $[\mathrm{H}^+]$ at a pH of 1.03 is 0.093 so $k_1 = 1350S$.

The value of $[\mathrm{H}^+]$ determined in this way equals the activity of the hydrogen ion since the pH was determined with a glass electrode. The values of [U(V)], however, are expressed in moles per liter so that the units of k_1 are moles^{-1} liter^{-1} sec.$^{-1}$ divided by the activity coefficient of the hydrogen ion in these solutions; this is in accord with the units employed for k_1 in all the earlier work.[3,8]

The increase in the rate constant with increase in temperature is plotted in Fig. 4 in terms of log S *vs.* $1/T$. The results are seen to fall on the straight line 9 within the limits of error. The activation energy, E, of the reaction calculated from the slope of line 9 equals 17.3 kcal. The value of k_1 is 135 at 25° as obtained from line 9 at $10^5/T = 335.5$. This value of k_1 at $\mu = 1$ agrees within our limits of error with the value of 300/2 = 150 for k_1 at $\mu = 0.5$ previously obtained in this Laboratory[3] when the U(V) was produced in the absence of air at 25° by the reaction between photoactivated uranyl ions and glucose instead of methanol and with the value of 130 ± 4 obtained for the disproportionation reaction of U(V) at the same pH but at $\mu = 0.4$ to 0.5.[8b,9]

The kinetic constants of the reaction are given in Table II. The half-lines of the observed reactions are given in Table I; the half-lines equal $1/[\mathrm{U(V)}_0 \text{-} 2k_1[\mathrm{H}^+] = 1/(D' - D_0)S$ and they, therefore, decrease with increase in the value of $D' - D_0$ even when the temperature, pH, and ionic strength are held constant.

The mechanism proposed[8b,c] for the reaction is

$$\mathrm{OUO}^+ + \mathrm{H}^+ = \mathrm{OUOH}^{+2} \qquad (a)$$

$$\mathrm{OUOH}^{+2} + \mathrm{OUO}^+ = \mathrm{OUOH}^+ + \mathrm{OUO}^{+2} \qquad (b)$$

$$\mathrm{OUOH}^+ \longrightarrow \text{stable U(IV) products} \qquad (c)$$

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[9] The value of 300 previously reported[3] for the rate constant at 25° should have been divided by two when compared with the previously published values[8b] of the rate constant, k_1, for the disproportionation of the U(V). This is revealed by the value given for k_1, in reference 8b. When this is done all the values of k_1 in perchlorate solution at 25° agree within the limits of error.

TABLE I

Concentrations, $[U(V)]_0$, of the intermediate U(V) species at instant photolyses were terminated and rates of the thermal disproportionation of this species into U(IV) and U(VI). The numbers given the expts. refer also to the plots of the results of these expts. in Figs. 3 and 4. The values of $D' - D_0$ and S are directly proportional to $[U(V)]_0$ and the rate constants of the disproportionation reaction, respectively. Values of A' are proportional to the extent of the photochemical reaction. The values of the light intensities, I, are relative. $(I/S)/(D' - D_0)^2 = 10500$ in all expts. except 1 and 3 where the values of $D' - D_0$ and therefore $[U(V)]_0$ are less than the steady state values. The values of $100 \cdot [U(V)]_0/[U(V)]_0^*$ give the concentration of the intermediate species at the end of the photolysis in terms of per cent. of the steady state value; the value in parentheses served as the basis for the theoretical values. The significance of x is explained in the text.

Expt.	°C.	I	$D' - D_0$	A'	10^2S	Half-life, sec.	x	100[U(V)]₀/[U(V)]₀* Expt.	Theory
1	14	7.6	0.10	0.13	3.2	313	0.9	67	72
2a	14	7.6	.15	.33	3.2	208	2.2	100	98
2b	14	7.6	.15	.61	3.2	208	4.2	100	99+
3	14	28	.19	.23	3.2	165	0.8	67	(67)
4a	14	28	.29	.38	3.2	108	1.4	100	88
4b	14	28	.29	.58	3.2	108	2.1	100	97
5	17-18	31	.24	.74	5.0	82.6	3.1	100	99+
6a	28-29	19	.115	.33	14	62.6	3.0	100	99+
6b	28-29	19	.115	.74	14	62.6	6.7	100	99+
7	35	33.7	.115	.16	25	35.4	1.5	100	90
8a	35	29.5	.105	.30	25	37.7	2.9	100	99+
8b	35	29.5	.105	.54	25	37.7	5.2	100	99+

TABLE II

KINETIC CONSTANTS OF THE U(V) SPECIES

The U(V) species thermally disproportionates into U(IV) and U(VI).

$$-d[U(V)]/dt = 2k_1[H^+][U(V)]^2$$

The values below were obtained in this research for aqueous perchlorate solutions at a pH of 1 and an ionic strength of unity when the [U(V)] is expressed in moles per liter, $p\text{H} = -\log [H^+]$ and the time is in sec. The value of k_1 in parentheses was obtained by interpolation as explained in the text. The symbols E, ΔH^*, ΔS^* and ΔF^* represent the activation energy, enthalpy, entropy and free energy of activation of the reaction; E covers the range 14 to 35° and ΔH^*, ΔS^*, ΔF^* are for 25°; $\Delta H^* = E - RT$ and $\Delta F^* = \Delta H^* - T\Delta S^*$. The Arrhenius factor A equals $k_1/e^{-E/RT} = e(kT/h)e^{\Delta S^*/R}$.

Temp., °C.	k_1	
14	43	$E = +17.3$ kcal.
17–18	68	$\Delta H^* = +16.7$ kcal.
25	(135)	$\Delta S^* = +8.3$ kcal.
28–29	190	$\Delta F^* = +14.2$ kcal.
35	340	$A = 6.5 \times 10^{14}$

The ion $OUOH^{+2}$ is believed[8] to be a strong acid whose ionization constant $1/K_a$ is greater than 10. Also the rate-determining step is believed[8] to be reaction (b). Accordingly at 25° our $k_1 = k_bK_a$ and $k_b \geq 1350$ (moles/l.)$^{-1}$ sec.$^{-1}$ compared to the value of 1300 published.[8b]

The kinetics of the reactions of uranium between its IV, V and VI states of oxidation appear to differ considerably from the corresponding reactions of neptunium. In the case of neptunium the equilibrium at pH 1 and 25° lies far on the side of the Np (V) state. The kinetics of the reaction between Np(IV) and Np(VI) is of the second order with respect to the activity of hydrogen ions and this has led to the supposition[10] that the disproportionation of Np(V) is also of the second order with respect to hydrogen ions instead of first order as in the case of U(V) since the equilibrium reaction

$$Me^{+4}(aq) + MeO_2^{+2}(aq) + 2H_2O = 2MeO_2^{+}(aq) + 4H^{+}(Aq)$$

appears to be common to both Np and U.

Part IV. Influence of Light Intensity and Temperature upon Steady State Concentration of the Intermediate U(V) Species.—The photostationary state concentration of the intermediate U(V) species is obtained by setting its rate of formation equal to its rate of decay. This situation can be taken to be established in expt. 2ab, 4ab, 6ab and 8ab since in Figs. 3 and 4 the lines 2, 4, 6 and 8 fit both the filled and unfilled circles representing the results of the a and b expt., respectively, which differ only in the values of A' as can be seen by reference to Table I. When the steady state prevails, the theory gives $+d[U(V)]/dt = 2\phi I = kI = -d[U(V)]/dt = 2k_1[H^+][U(V)]^2 = {}'k[D' - D_0]^{*2}$ where k and $'k$ are constants at constant ϕ, acidity, ionic strength and temperature. The asterisk denotes the steady state value.

The theoretical influence of the light intensity upon the steady state concentration of the intermediate species is given by the equation

$$(D' - D_0)^* = (kI/{}'k)^{1/2} = a\sqrt{I}$$

where a is constant when ϕ and $'k$ (or S) are constant. The test of this equation is provided by expt. 2ab and 4ab. In these expt. the data agree with the equality $(D' - D_0)_4^*/(D' - D_0)_2^* = 0.29/0.15 = 1.9 = \sqrt{I_4/I_2} = \sqrt{28/7.6}$ thereby confirming the theoretical influence of the light intensity and rate of formation of the intermediate species upon the steady state concentration of this species.

The theoretical influence of temperature upon the steady state is given by the equation

$$(D' - D_0)^* = (kI/{}'k)^{1/2} = b\sqrt{I/S}$$

where b is constant when ϕ is constant. The test of this equation is provided by the equality of $(D' - D_0)_i^*/(D' - D_0)_2^*$ and $[(I/S)_i/(I/S)_2]^{1/2} =$ 1.92, 1.61, 0.756, 0.760 and 0.707, respectively, in the case of expt. 4, 5, 6, 7 and 8 compared to expt. 2. These expt. cover the temp. interval of 14 to 35° which increased S from 0.032 to 0.25 or about eightfold. The agreement of the data with the above equality and the constancy of the value of $(I/S)/(D' - D_0)^{*2} = 10{,}500$, as noted in the legend of Table I, completely confirms the stationary state theory with respect to the influence of both the rate of formation and decay of the intermediate species upon the steady state value of this species.

It seems worthwhile to point out that the magnitude of the steady state concentration of the intermediate species and of the after-effect as measured in these expt. by $(D' - D_0)^*$ is increased by circumstances increasing the rate of formation of the intermediate species, as in expt. 2 and 4 by increasing the light intensity and by circumstances decreasing the rate of decay of the intermediate species as in expt. 8 and 4 by decreasing the temperature.

Part V. Influence of Extent of Reaction, Light Intensity and Temperature upon Build-up of Concentration of the Intermediate Species.—The

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(10) J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, 76, 3278 (1954).

build-up of the concentration of the intermediate U(V) species responsible for the after-effect is given according to theory by the equation

$$d[\mathrm{U(V)}]/dt = 2\phi I - 2k_1[\mathrm{H}^+][\mathrm{U(V)}]^2 = kI - {}''k[\mathrm{U(V)}]^2$$

where k and $''k$ are constants in these expts. when the temperature is constant. The solution of this equation is

$$t = (1/''kkI)^{1/2} \tanh^{-1} [\mathrm{U(V)}]/(''k/kI)^{1/2}$$

where t is here the duration of the photolysis. The constant of integration is zero since $[\mathrm{U(V)}]_0 = 0$ when $t = 0$. The steady state value of [U(V)] is obtained by setting $d[\mathrm{U(V)}]/dt = 0$ and then $(''k/kI)^{1/2} = [\mathrm{U(V)}]_0^*$. Thus $[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^* = \tanh x$ where $x = t(''kkI)^{1/2}$. The plot of $[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^*$ (or $[D' - D_0]/[D' - D_0]^*$) *vs.* x is given in Fig. 5.

The theoretical influence of the extent of the photochemical reaction upon the extent of the build-up of the concentration of the intermediate species is obtained by relating A', $[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^*$ and x. The values of x and A' are related as follows

$$A'/\epsilon_4 = t\phi I = x^2/''kt;\ \text{hence}\ x_1/x_2 = (A'_1/A'_2)[(''k/I)_1/(''k/I)_2]^{1/2}$$

The value of A' corresponding to a stated value of x is most precisely and simply obtained by evaluating experimentally the corresponding values of $(D' - D_0)/(D' - D_0)^*$ and A' under conditions where in one case the D ratio substantially differs from unity and in the other case practically equals unity. The value of x corresponding to the lower value of $(D' - D_0)/(D' - D_0)^*$ is then read off Fig. 5 and thereafter the corresponding values of x and A' can be calculated from the above equation for x_1/x_2.

The test of the theory regarding the influence of the extent of reaction, A', upon the value of $D' - D_0$ is provided by expt. 1 and 2 at a low value of I and by expt. 3 and 4 at a high value of I. In expt. 2 and 4, $D' - D_0$ appears to be at the steady state value since $D' - D_0$ remained unchanged in the a and b expt. of the same number when A' was increased nearly twofold. But in expt. 1, $D' - D_0$ is 67% and A' is 41 and 22% of the corresponding values in expt. 2a and b all at the same low value of I; and in expt. 3, $D' - D_0$ is 66% and A' is 59 and 39% of the corresponding values in expt. 4a and b all at the same higher value of I. In expt. 1 and 3, therefore, $(D' - D_0)/(D' - D_0)^* = [\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^* = 0.67$ and from Fig. 5 the corresponding value of x is about 0.8. The values of A' in expts. 2a and b compared to expt. 1, therefore, correspond to values of 2.0 and 3.7 for x and of 96 and 99.9% for $[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^*$ compared to the observed values of 100% for $(D' - D_0)/(D' - D_0)^*$; similarly the values of A' in expt. 4a and b compared to expt. 3 correspond to 1.4 and 2.1 for x and to 88 and 97% for $[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^*$ compared to observed values of 100% for $(D' - D_0)/(D' - D_0)^*$. The agreement of the experimental results with theory is within 4% except in expt. 4a where the difference is 12%; this difference, however, is reduced to 8% if x is increased from 1.4 to 1.55 which corresponds to an error of 5% in the values of A' as was usually the case.

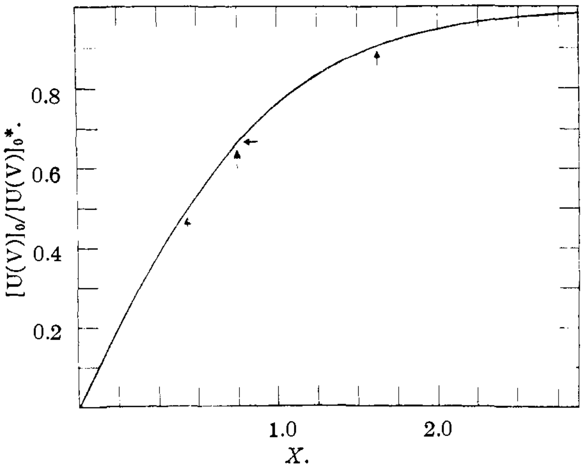

Fig. 5.—Curve showing the build-up in the concentration of the intermediate U(V) species to its steady state value as the photochemical reaction progressed. The ordinate represents the ratio of the actual concentration of this species to the steady state value; this ratio equals $(D' - D_0)/(D' - D_0)^*$ where the star designates the steady state value. The abscissa, x, is proportional to the extent of the photochemical reaction; the mathematical relationship between x and the measurable variables is given in the text.

The curve approaches asymptotically the steady state value as x approaches infinity. The single arrows point to one-half and 90% of the steady state value where $x = 0.55$ and 1.5, respectively. The double arrows point to the value obtained for the ratio of the $D' - D_0$ values in expt. 3 compared to 4; this point served as the basis of comparison of the experimental and theoretical values of $100[\mathrm{U(V)}]/[\mathrm{U(V)}]^*$ listed in Table I.

The influence of the light intensity, I, upon the value of A' corresponding to a given value of x is revealed by expt. 1 and 3 for which the values of x are equal because the values of $(D' - D_0)/(D' - D_0)^*$ are equal, hence $(I_1/I_3)^{1/2}$ should equal A'_1/A'_3 since the temperature and, therefore, $''k$, is constant. The experimental value of $I_1/I_3 = 7.6/28$ and the square root equals 0.52 which is to be compared to $A_1'/A_3' = 0.133/0.226 = 0.59$. In expt. 2 and 4, the value of the square root of I_2/I_4 is also 0.52 but since x does not have the same value in both expts. the value of 0.52 is now to be compared to $A_2'x_4/A_4'x_2 = 0.59$ and 0.60 in the case of 2a/4a and 2b/4b, respectively. The values of 0.52 and 0.59 differ by 14% but this difference becomes negligible if the errors in A and I are about 5% as was usually the case.

The test of the theory regarding the influence of temperature upon the extent of reaction A' required to attain certain fractions of the steady state value is provided by a comparison of the expt. at 14°, 17–18°, 28–29° and 35°. The basis for this comparison is taken to be expt. 3 since in this expt. x quite clearly equals 0.8 when $A' = 0.226$ and the relative values of I and S are 28 and 0.032, respectively. The values of x in the other expt. are then given by the equation $x = (0.8/0.226)(28/3.2)^{1/2}A'(S/I)^{1/2} = 10.5A'(S/I)^{1/2}$. The values of $100[\mathrm{U(V)}]_0/[\mathrm{U(V)}]_0^*$ corresponding to the values of x calculated on this basis were obtained from Fig. 5 and are listed in Table I under theory. They are seen to agree with the experimental values calculated from $D' - D_0$ within the limits of error. The experimental results, therefore, are self-consistent and confirm the steady state theory in every detail regarding the influence of the extent of reaction, light intensity and temperature upon the steady state concentration of the intermediate species and the build-up and decay of the concentration of this species.

It seems worthwhile to distinguish between the duration, t, and extent, A', of photolysis required to attain a given value of x and consequently a given fraction of the steady state value. Consider the equations $t = x/(''k\phi I)^{1/2}$ and $A' = x(\phi I/''k)^{1/2}$. The first of these equations shows that the duration of the photochemical reaction required to reach a stated value of x or fraction of the steady state is decreased by increasing either the temperature (*i.e.*, $''k$) or the light intensity, I, or the quantum yield, ϕ, or all of them. The decrease in this time is seen to be inversely proportional to the square root of the per cent. increase in these variables. The second of these equations shows that the extent of photolysis required to reach a stated value of x or fraction of the steady state is decreased by increasing the temp. (*i.e.*, $''k$) but that the opposite effect is obtained by an increase in light intensity or quantum yield or both. It follows that both the time and extent of photolysis required to reach within 1 or 10% of the steady state becomes smaller the larger the rate of decay of the intermediate species, *i.e.*, the shorter the after-effect and *vice versa*.

In the case of reactions in which the intermediate species is thermally produced as well as destroyed, $2\phi I$ is replaced by the thermal rate of formation of the intermediate species so that again both the time and extent of reaction required to establish the steady state will be small when the rate of decay is large and the steady state concentration of the intermediate species is small.

Finally the results of this research show that one can deal satisfactorily in a simple way with the kinetics of photochemical reactions involving intermediate species even when the actinic light is strongly absorbed by a thin layer of the solution next to the wall of the reaction vessel provided the solution is adequately stirred and provided the actinic light is monochromatic and one knows or holds constant the fraction of this light absorbed by the photosensitive species.

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Thermal Conductivities of Condensed Gases. I. The Thermal Conductivity of Liquid Nitrogen between 65 and 90°K.

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A cell for measuring the thermal conductivity of liquids at low temperatures is described in this paper. Data on the conductivity of liquid nitrogen from 65 to 90°K are presented. These data are considerably lower than those of Hammann[1] (1938) and compare closely with those given by Borovik, Matveev and Panin[2] (1940). Our research, as well as that of Hammann, employed the parallel plate arrangement; whereas measurements made by Borovik, Matveev and Panin were made by using a radial flow type of cell.

Introduction

Previously published data on the thermal conductivity of liquid nitrogen display great inconsistency. For example, Hammann,[1] whose measurements cover the range 64.7–73.5°, reported a thermal conductivity coefficient, K, of 4.96×10^{-4} cal. cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$ at 73°K.; whereas the data of Borovik, Matveev and Panin[2] for the range 77.9–111.8°K. lead to an extrapolated value of 3.9×10^{-4} at 73°K. Moreover, Hammann found K to be practically independent of temperature; whereas Borovik, Matveev and Panin report that the conductivity decreases at a constant rate with temperature. Consequently, we were led to reinvestigate the conductivity of liquid nitrogen at low temperatures, as part of a program, in this Laboratory, for measuring the thermal conductivities of condensed gases.

Apparatus.—The conductivity cell used in this work is of the parallel plate type. A line drawing of our cell is shown in Fig. 1. Essentially, it consists of a thin-walled cylindrical container for the liquid under study, which is heated at a measured rate at its upper end and is in thermal contact with a constant-temperature cryostating bath at its lower end. A multiple-junction-difference thermocouple is used to determine the thermal gradient through the liquid.

The Measuring Cell.—The cell wall, A in Fig. 1, is made of No. 26 gage stainless steel, type 302, and has an internal diameter of 3 in. and a length of 1 in. Its top is soft-soldered onto a nickel disk, B, whose lower surface is grooved to fit it. The disk serves as a heating plate and its upper surface is grooved to hold a pancake heater of 40 ohms of No. 30 B and S insulated manganin wire. The lower end of the cell wall is soft-soldered into a circular groove in the nickel-plated upper surface of a thick copper plate, C.

The tube D, which leads the liquid into the chamber through a small hole in the center of the heater plate, is usually filled with liquid during an experiment. To prevent convection, a cylindrical copper block, E, wrapped with a heating coil, is placed in the tube line, $1^5/_8$ in. above the heater plate. During an experiment it is maintained, when possible, at the temperature of the pancake heater. Besides preventing convection in the entrant tube, the block traps out any heat that tends to flow to the heater, B, through thermocouples and heater leads from outside the apparatus, and also prevents the measuring chamber from "seeing" parts of the apparatus at room temperature. Heat is leaked away from this block through five short lengths of No. 12 braided copper wire, soldered at one end to the top of the block and at the other end to the $^3/_4$-in. monel tube, F, which is immersed in the cryostating bath.

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(1) G. Hammann, *Ann. Physik*, **32**, 593 (1938).

(2) E. Borovik, A. Matveev and E. Panin, *J. Tech. Phys.* (*USSR*), **10**, 988 (1940).