mole^{-1}, respectively, at 298.16°K. These heats of formations lead to $\Delta H^{\circ}_{298\cdot16}$[14] $= -669 \pm 45$ cal. The close agreement between the calorimetric heat and that calculated from $\partial \ln K_1/\partial\, 1/T$ substantiates our conclusion that the free energy difference between UH_3 and UH_2D does not appreciably depend on the relative amounts of α and β forms of UH_3.

Acknowledgment.—We thank Mr. A. P. Irsa of this Laboratory for carrying out the mass spectrometer analyses. We also wish to thank Dr. B. M. Abraham and Mr. H. Flotow of the Argonne National Laboratory for sending us the results of their calorimetric measurements prior to publication. In addition it is a pleasure to acknowledge a stimulating conversation with Dr. Abraham on the heats of formation of the isotopic uranium hydrides.

UPTON, L. I., N. Y.

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Kinetics of the Exchange of Water between $Cr(H_2O)_6^{+3}$ and Solvent

BY JOHN P. HUNT AND ROBERT A. PLANE

RECEIVED JULY 1, 1954

Measurements of the exchange of water between solvent and $Cr(H_2O)_6^{+3}$ have been extended to dilute solution. The rate is best expressed as rate $= k_1(Cr(H_2O)_6^{+3})$ over a wide range of ionic strength. k_1 increases slightly with ionic strength and has an average value at infinite dilution of 2.07×10^{-4} min.$^{-1}$ at 27° in both nitrate and perchlorate solutions. An activation energy of 27.6 kcal./mole is found at 0.7 molar ionic strength.

Investigation of the rate of substitution of water for water in aquo ions is of fundamental importance in understanding substitution reactions in complex ions. A start has been made by studying the water exchange reaction of $Cr(H_2O)_6^{+3}$.[1,2] These studies, limited to concentrated solutions, suggested the rate law: rate $= k_2(Cr(H_2O)_6^{+3})$(anion). Values of k_2 were surprisingly independent of ionic environment. The present authors have extended the measurements to more dilute solutions enabling more rigorous testing of rate laws. As has been pointed out,[1] comparisons of rates of water exchange with rates of complex ion formation reactions can give information regarding mechanisms and the present data should be more useful in this connection.

Experimental

The general procedure and methods have been described previously.[2] H_2O^{18} again was used as the tracer.

The significant innovation in experimental procedure involved sampling by precipitation and ignition of $CrPO_4 \cdot 6H_2O$. The basic process used was as follows. To 10 ml. of solution at room temperature and 0.1 *M* in Cr^{+3}, 0.1 *M* in H^+ was added solid $NaH_2PO_4 \cdot H_2O$ in 10% excess with vigorous stirring. After solution occurred (*ca.* 1 min.) solid $NaC_2H_3O_2$ was added until the *p*H was 5. The resulting slurry was stirred 5 min., the lavender solid filtered on a Hirsch funnel, washed 5 times with ordinary distilled water, and dried 20 min. by sucking air through the filter. The powder was further dried over $CaSO_4$ in a vacuum desiccator for 40 min.

Modification of the precipitation was necessary when Cr^{+3} was < 0.1 *M* or $H^+ > 0.1$ *M* or total anion concentration > 1.0 *M*. For some samples dilution with ordinary distilled water was sufficient to obtain the basic conditions. If Cr^{+3} was < 0.1 *M*, Na_2HPO_4 replaced $NaH_2PO_4 \cdot H_2O$. With $H^+ > 0.1$ *M* or anion concentration > 1.0 *M* after dilution to 0.1 *M* Cr^{+3}, Na_2HPO_4 again replaced $NaH_2PO_4 \cdot H_2O$.

Chemical analyses of the dry solids showed that they were indeed $CrPO_4 \cdot 6H_2O$.

Tracer experiments showed that *ca.* 1% "induced exchange" occurred during precipitation, the amount of exchange being reproducible with constant conditions of precipitation, varying slightly from run to run as these conditions changed.

The ignition of $CrPO_4 \cdot 6H_2O$ to $CrPO_4 + 6H_2O$ was carried out as follows: 0.25 g. in a small Pt boat was placed in a horizontal Pt crucible. The latter was inserted in a horizontal Vycor tube which was then attached to a vacuum line. The Vycor tube could be heated by means of a tube furnace. Next, the solid was outgassed for 20 min. by pumping at 10^{-5} mm. Dry, oxygen-free, N_2 was then admitted to 1 atm. pressure (this was necessary to prevent loss of sample from the boat during the initial heating). The temperature of the sample was raised to 160° in 15 min. following a time schedule, then held constant at 160° for 20 min. *Ca.* $4H_2O/Cr$ had been evolved at this stage and collected in a cool portion of the Vycor tube. The N_2 and H_2O were pumped off through a −180° trap, collecting the H_2O. Ignition was continued at 10^{-5} mm., raising the temperature to 750° in 30 min. according to a fixed time schedule. This temperature was maintained for 10 min. The final $2H_2O/Cr$ were trapped out continuously during this 40-min. period. Total H_2O was transferred to a sample tube and equilibrated with CO_2 for mass spectrometer analysis.[2]

Tracer studies showed that exchange of oxygen between phosphate and H_2O occurred above 160°. Because of this, $15.2 \pm 0.4\%$ of the oxygen in the final sample was derived from phosphate.

Materials.—Chromic perchlorate was made by reducing CrO_3 in $HClO_4$ with 30% H_2O_2. Excess H_2O_2 was destroyed by heating in the presence of platinized Pt. The solution was evaporated to crystals and these were recrystallized from H_2O. Another source of the chromic salt was commerical reagent recrystallized from H_2O. Results were independent of the source of the salt. Sodium perchlorate was made from NaOH and $HClO_4$.[3] $(C_2H_5)_4NBr$ was recrystallized from absolute C_2H_5OH. All water was redistilled from alkaline permanganate and then from Pyrex. The 1.5% H_2O^{18} used was purchased from the Stuart Oxygen Company through the A. E. C. Starting materials were the best commercial grades available used without further purification unless noted above.

Treatment of Data.—The rate of the chemical reaction producing the isotope exchange was calculated from the mass spectrometer data by methods described previously.[2] All calculations ignore isotope effects on the rate.

Values of k_1 reported are based on the expression: rate $= k_1(Cr(H_2O)_6^{+3})$, and those of k_2 on the expression: rate $= k_2(Cr(H_2O)_6^{+3})$ (anion). The concentration of H_2O could not be varied sufficiently or independently enough to justify inclusion in rate laws. The *k*'s as calculated refer to the exchange of all $6H_2O$.

All concentrations are expressed in molar units. μ refers to molar ionic strength.

---

(1) J. P. Hunt and H. Taube, *J. Chem. Phys.*, **19**, 602 (1951).

(2) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(3) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 72.

Results

The data obtained are summarized in Table I.

TABLE I

KINETIC DATA

$[Cr(ClO_4)_3]$	$[HClO_4$	μ	T, °C.	$t^1/_2$, hr.	$k_1 \times 10^4$, min.$^{-1}$ 27°	$k_2 \times 10^4$, min.$^{-1}$ 27°
0.0495	0.0990	0.396	27.53	53.0	2.00	8.10
.0954	.0968	.669	27.53	51.8	2.03	5.30
.0960	.0956	.672	27.53	51.8	2.03	5.29
.0978	.0996	.687	34.53	18.8	2.03	5.19
.0985	.504	1.095	34.53	18.9	2.03	2.54
.1015	.1003	1.349[a]	34.53	17.9	2.14	2.05
.3025	.1031	1.918	34.53	17.3	2.16	2.14
.4264	.4156	2.974	27.58	45.0	2.23	1.32
.1113	.1130	4.302[b]	27.53	35.0	3.00	0.76
1.085	.3759	6.886	27.58	28.0	3.28	0.90
0.1041[c]	.1027[c]	0.727	27.58	44.5	2.36	5.69
0.0969[c]	.0956[c]	4.012[d]	27.58	58.0	1.78	

[a] Contained 0.640 *M* $NaClO_4$. [b] Contained 3.521 *M* $NaClO_4$. [c] NO_3^- substituted for ClO_4^-. [d] Contained 3.335 *M* $(C_2H_5)_4NBr$.

The largest sources of error in these results arise from the "induced exchange" and exchange during ignition previously mentioned. On the basis of precision a maximum uncertainty of ±4% in the rate was assigned. This represents a significant improvement in precision over the earlier data.

The experiment at $\mu = 6.886$ is essentially a repeat of no. 4a, 4b and II reported by Plane and Taube.[2] The measured half-times are in good agreement suggesting the reliability of the new sampling procedure.

Comparison of the 4th and 5th experiments in Table I reveals no appreciable effect of H^+ concentration on the half-time of reaction in agreement with the earlier observations.

From the third and fourth experiments in the table an activation energy of 26.7 kcal./mole was obtained. On the basis of the precision of the individual rate constants an uncertainty of ±1 kcal./mole is assigned. This value of the activation energy was used for calculations of the reported k's at 27.00°. The previous value, at much higher concentrations, was 26 ± 2 kcal./mole in the same temperature range.

From Fig. 1 it is seen that the value of k_1 at $\mu = 3.14$ obtained previously is not on a reasonable curve of the data. The eighth experiment in Table I was done to check this point and the result is in good agreement with the bulk of the data. No explanation can be offered for the earlier observation.

Discussion

In contrast to the observations at high concentrations only, application of the rate law: rate = $k_2(Cr(H_2O)_6^{+3})$(anion) to the total data yields values of k_2 which vary widely with conditions. The Brönsted–Bjerrum theory predicts the ionic environment effect to be given by: $k = k_0\gamma_{Cr^{+3}}(\gamma_{\text{anion}}/\gamma^*)$, where γ^* refers to the activity coefficient of the activated complex (Cr anion)$^{*\,+2}$ essentially at infinite dilution in the solution. No activity data are available for the perchlorate system, but data exist for $Cr(NO_3)_3$ and nitrates of some +2 ions. These data can be quite well represented up to 1 molal by Guggenheim's equation[4]

$$\ln \gamma_{\pm}(R,X) = -\alpha Z_+|Z_-|\sqrt{I}/1 + \sqrt{I} + 2\beta(R,X)\bar{\nu}m$$

To take into account the effect of the presence of several electrolytes Guggenheim's mixture equation was applied.[5] This treatment predicts that k_2 should decrease by 30% in the region $\mu = 0.6$ to 4.0. The observed values for NO_3^- decrease by a factor of 4 and for ClO_4^- by a factor of 7. On this basis, the rate law seems unreasonable. Clearly an unambiguous conclusion requires data and theory not now available.

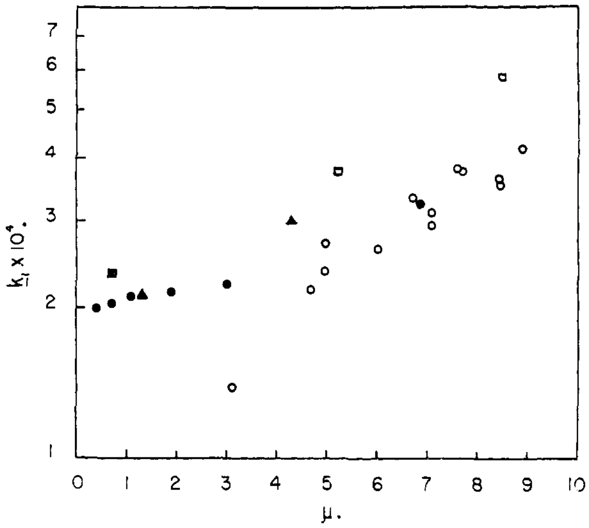

Fig. 1.—First-order rate constants at 27° as a function of molar ionic strength. Circles denote experiments in ClO_4^- solutions; squares NO_3^- solutions; triangles experiments with $NaClO_4$. Filled symbols refer to present results; open symbols to previous data.

The over-all data can be represented more simply and more reasonably by the expression

$$\text{rate} = k_1(Cr(H_2O)_6^{+3})$$

Figure 1 shows that k_1 increases as μ increases and that the effect is not large considering the range of μ values. In the present case the above rate law does not distinguish a rate-determining step in which dissociation of $Cr(H_2O)_6^{+3}$ first occurs, from one in which H_2O attacks the $Cr(H_2O)_6^{+3}$ to form a 7-coördinated intermediate. In neither case would a change in charge be involved in the rate-determining process, thus no large effect of ionic environment is expected.

For the dissociation mechanism the perchlorate data are rationalized if the ratio of the γ's of the two +3 ions involved change by a factor of *ca.* 2 over the range $\mu = 0$ to $\mu = 9$. This corresponds to a change in ratio of $\gamma_{\pm}$'s for the corresponding salts by a factor of $2^{1/4}$, a quite reasonable effect. The corresponding change required in $\gamma_{\pm}$'s for the nitrates would be a factor of *ca.* $3^{1/4}$, again reasonable.

If the 7-coördinated mechanism is to hold, the above remarks are modified by including the activity of H_2O which must decrease with in-

---

(4) E. A. Guggenheim, "Thermodynamics," Interscience Publishers, Inc., New York, N. Y., 1949, p. 314.

(5) *Ibid.*, p. 315.

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.

ITHACA, NEW YORK

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Photostationary State Kinetics[1]

BY LAWRENCE J. HEIDT

RECEIVED AUGUST 2, 1954

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

---

(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).