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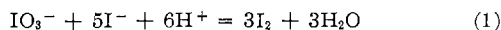
Rate of the Dushman Reaction at Low Iodide Concentrations. Experimental Method and Temperature Coefficient

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To obtain information needed for the eventual explanation of the oscillating decomposition of hydrogen peroxide in acid iodate-iodine systems, it is necessary to reinvestigate the Dushman reaction (reduction of iodate by iodide in acid solution) at iodide concentrations below $10^{-7} M$ and to measure its temperature coefficient. Measurements were made of rates kept constant by the maintenance and interaction of three equilibria in which $AgI(s)$, $AgIO_3(s)$, and HIO_3 are involved. A new experimental method was devised, tested, and found satisfactory. Specific rates, corrected for equilibrium salt effects, are given for 15, 25, and 50°. At 25°, measured rates are higher than corresponding values based on earlier work by a similar method, and they fall near corresponding rates based on two investigations of radioactive exchange between I_2 and IO_3^- . It appears likely that the Dushman reaction influences the oscillating decomposition of hydrogen peroxide.

The Dushman reaction,¹ classical in chemical kinetics, is



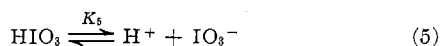
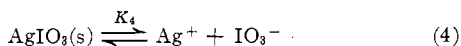
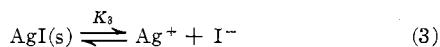
It was found by Abel and Hilferding² to have the rate law

$$+^{1/3}d[I_2]/dt = -d[IO_3^-]/dt = k_2[IO_3^-][I^-][H^+]^2 \quad (2)$$

at 25° and $[I^-]$ below $10^{-7} M$.

At 50°, the oscillating decomposition of H_2O_2 exhibits pulses in $[I^-]$ at these low concentrations.³ The present investigation was undertaken to establish whether the Dushman reaction needs to be considered in explaining the oscillating decomposition. The experimental method of Abel and Hilferding had to be modified in several important respects.

The rate measurements are difficult to make because $[I^-]$ is so low. As carried out, they assume virtual establishment of the three equilibria



In 1928, HIO_3 was considered a strong acid; Abel and Hilferding thus did not take equilibrium 5 into account.

Having two solids in equilibrium with a common ion is expected to maintain $[I^-]$ at a constant value given by⁴

$$[I^-] = [IO_3^-]K_3/K_4 \quad (6)$$

So long as $[IO_3^-]$ and $[H^+]$ are large enough so that they do not change appreciably during the course of reaction 1, this reaction will proceed at constant rate, and

$$k_2 = {}^{1/3}K_4/K_3 \left\{ \frac{\Delta[I_2]}{\Delta t} / [H^+]^2[IO_3^-]^2 \right\} \quad (7)$$

These conditions obtained in our experiments.

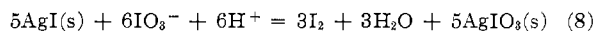
(1) S. Dushman, *J. Phys. Chem.*, **8**, 453 (1904).

(2) E. Abel and K. Hilferding, *Z. Phys. Chem.*, **136**, 186 (1928).

(3) I. Matsuzaki, J. H. Woodson, and H. A. Liebhafsky, *Bull. Chem. Soc. Jap.*, **43**, 3317 (1970), and other references there cited.

(4) Units throughout are moles, liters, minutes. Variables that express composition need special attention. Brackets are used to denote concentrations of $HClO_4$ and of $NaIO_3$ added to make the reaction mixture—or of their ions, complete dissociation being assumed. For iodide, brackets mean "calculated according to eq 6;" for I_2 , they mean "concentration that would be spectrophotometrically measured." Other concentrations actually existing, or calculated actually to exist, in the reaction mixture are denoted by parentheses. Equation 6 tacitly assumes that differences in the two anionic activity coefficients are negligible.

After $AgIO_3(s)$ begins to form, reaction 1 becomes



a point not mentioned by Abel and Hilferding.

Final Experimental Method.—It is difficult to maintain $[I^-]$ near the equilibrium concentration $[I^-]_e$ of equilibrium 3 and to cope with other difficulties associated with $AgI(s)$. We believe the following (final) experimental method to be satisfactory.

The reaction vessel was a thermostated 125-ml erlenmeyer flask with numerous punched indentations to give turbulent flow. Stirring at a rate near 1600 rpm was accomplished with a variable-speed electric stirrer operating through a mercury seal. A 30-g amount of reagent quality $AgI(s)$, the required volume of $NaIO_3$ solution, and enough dissolved $AgNO_3$ to make the reaction mixture (final volume of solution 100 ml) $10^{-3} M$ in Ag^+ were placed in the reaction vessel and stirred. The required volume of $HClO_4$ solution was added to start reaction.

Ten seconds prior to t , the time of a sample, stirring was stopped and the solids were allowed to settle, a proved procedure for halting the reaction. With a syringe, 3 ml of solution was then withdrawn and discharged into a small separatory funnel that contained 4 ml of CCl_4 . After the iodine had been extracted by vigorous shaking for 3 min, the CCl_4 was transferred to a cuvette that was centrifuged for 90 sec prior to the spectrophotometric determination of I_2 at 5000 Å. Blank experiments with known amounts of I_2 showed the procedure to be satisfactory.

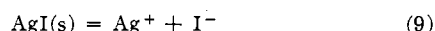
Solid iodine was never formed in our experiments. By the final method, "old" and "new" $AgI(s)$ gave the same results, "old" $AgI(s)$ having been used in one or more previous experiments and therefore containing the reaction product $AgIO_3(s)$.

Problems with Silver Iodide.—First, there must be no direct oxidation of $AgI(s)$, for this would contravene eq 2. Neither Abel and Hilferding nor we encountered such oxidation.

Second, the $AgI(s)$ must contribute no reactive impurity, a stringent requirement in light of the 300 g/l. used in our final method. In preliminary experiments with "new" $AgI(s)$, formation of excess iodine during the initial period of reaction was usually observed at rates sharply exceeding the constant rate expected and attained after this initial period (some-

times 60 min long or more) was over. The anomaly was eventually ascribed to a trace of soluble iodide in the AgI(s). In any event, the anomaly disappeared when AgNO₃ was initially added as prescribed above: the observed rates were then constant to within the experimental error (except as noted below) from $t = 0$ onward.

Third, the AgI(s) should give no long induction period if it dissolves rapidly to establish equilibrium 3. During the induction period, reaction 1 will proceed at decreasing rate until reaction 8 takes over. The length of the induction period with "new" AgI(s) can be estimated as follows. Upon mixing of the reagents, the reaction



will proceed until enough Ag⁺ has formed to establish equilibrium 4. The increase in [Ag⁺] will measure all the iodide formed in reaction 9. At $t = 0$, [I⁻] = $\sqrt{K_3}$. Call this concentration a , and let x be the [Ag⁺] added to the reaction system by reaction 9 in time t . Then $a + x = [\text{Ag}^+]$ at time t , $K_3/(a + x) = [\text{I}^-]$ at time t , and $K_4/[\text{IO}_3^-] = [\text{Ag}^+]$ when equilibrium 4 is reached (effect of equilibrium 5 neglected). From eq 2

$$d(a + x)/dt = 5k_2[\text{H}^+]^2[\text{IO}_3^-]K_3/(a + x) = (\text{constant})[\text{IO}_3^-]/(a + x) \quad (10)$$

which gives

$$\int_a^{K_4/[\text{IO}_3^-]} (a + x)d(a + x) = (\text{constant})[\text{IO}_3^-] \int_0^t dt \quad (11)$$

and

$$t = \frac{1/2\{(K_4)^2/[\text{IO}_3^-]^3 - a^2/[\text{IO}_3^-]\}}{\text{constant}} \quad (12)$$

where "constant" is defined by eq 10. The induction period t varies inversely as $[\text{H}^+]^2$ and almost inversely as $[\text{IO}_3^-]^3$. According to this treatment, the rate of iodine formation decreases during an induction period not over several minutes long. This behavior is in accord with detailed data for all final—but not for all preliminary—experiments; see Figure 1. The success

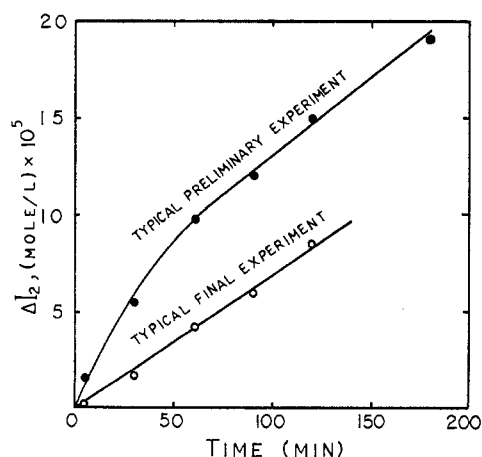


Figure 1.—Detailed results of two experiments.

of the treatment increases confidence in the final experimental method and the final results.

Fourth, AgI(s) must dissolve rapidly enough to ensure the virtual maintenance of equilibrium 3 even when iodine is being formed at the maximum constant

rate. Experiments were done over the entire temperature range to establish the AgI(s) content beyond which k_2 no longer increased when more of the solid was added. This amount was near 100 g/l. Three times that much was used in the final method. If AgI(s) does not dissolve fast enough, [I⁻] will fall below the equilibrium value used to calculate k_2 . The calculated result would then be too low. This is one reason for placing more confidence in the higher values of k_2 .

Finally, the rate of solution of AgI(s) should be independent of time. Owing to the violent stirring, the finely divided iodide gradually adsorbs air and eventually floats on the liquid when stirring is interrupted. We interpret a decrease in the rate of iodine formation sometimes observed near the end of long experiments as due to a decreased rate of solution of AgI(s) owing to adsorbed air. A reliable value of k_2 was always obtained before any such decrease occurred.

Problems with Iodic Acid.—Iodic acid is an *intermediate electrolyte*, neither weak nor strong. It can form ions that contain more than one iodine atom.^{5,6} Undissociated HIO₃ exists; (H⁺) and (IO₃⁻) consequently are smaller than [H⁺] and [IO₃⁻]. In our reaction system, there is a further problem. Because (IO₃⁻) is less than [IO₃⁻], (I⁻) must also be less than [I⁻]; see eq 6. We have

$$K_5 = (\gamma_{\pm})^2(\text{H}^+)(\text{IO}_3^-)/(\text{HIO}_3) \quad (13)$$

if the activity coefficient of HIO₃ is unity. Mean ionic activity coefficients for our reaction mixtures not being available, we have substituted those for perchloric acid solutions of the same ionic strength. See below.

With (IO₃⁻) from eq 13, we have calculated (I⁻) as in eq 6 and obtained a *corrected* specific rate k_2' from

$$k_2' = k_2[\text{I}^-]/(\text{I}^-) \quad (14)$$

This calculation corrects for the effect of equilibrium 5 on equilibrium 3.

Evaluation of Needed Equilibrium Data.—We have evaluated K_3 , K_4 , and K_5 over the temperature range 0–50° from data in the literature. For K_3 and K_4 , we have used data from two compilations^{7,8} to obtain the equations

$$\log K_3 = -(6.000 \times 10^3/T) + 4.068 \quad (15)$$

$$\log K_4 = -(3.040 \times 10^3/T) + 2.714 \quad (16)$$

For K_5 , literature data^{5,6,9} are the basis for our equation

$$\log K_5 = +(0.633 \times 10^3/T) - 2.904 \quad (17)$$

Obviously, the dissociation of HIO₃ is exothermic.

For calculations involving eq 13, γ_{\pm} for HClO₄ at 25° was used¹⁰ at all temperatures. The equation was solved by making successive approximations to obtain self-consistent values of concentrations, activity coefficients, and ionic strengths.

(5) E. Abel, O. Redlich, and P. Hersch, *Z. Phys. Chem., Abt. A*, **170**, 112 (1934).

(6) A. D. Pethybridge and J. E. Prue, *Trans. Faraday Soc.*, **63**, 2019 (1967).

(7) L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17**, 339, 350 (1964).

(8) W. F. Linke, "Solubilities, Inorganic and Metal-Organic Compounds," 4th ed, Van Nostrand, New York, N. Y., 1958, pp 93 and 101.

(9) N. C. C. Li and Y. Lo, *J. Amer. Chem. Soc.*, **63**, 397 (1941).

(10) "Handbook of Chemistry and Physics," 51st ed, Chemical Rubber Co., Cleveland, Ohio, 1970, p D-123.

TABLE I
 FINAL RESULTS AT THREE TEMPERATURES^a

No.	[HClO ₄]	[NaIO ₃]	(γ_{\pm}) _{HClO₄}	(H ⁺)	(IO ₃ ⁻)	(HIO ₃)	10 ⁻⁴ k ₂	10 ⁻⁴ k ₂ '
15°, K ₃ = 1.742 × 10 ⁻¹⁷ , K ₄ = 1.416 × 10 ⁻⁸ , K ₅ = 0.195								
1	0.50	0.20	0.776	0.390	0.090	0.110	3.08	6.87
2	0.797	0.20	0.802	0.659	0.062	0.138	2.69	8.62
3	0.50	0.25	0.778	0.367	0.117	0.133	2.84	6.01
25°, K ₃ = 8.591 × 10 ⁻¹⁷ , K ₄ = 3.199 × 10 ⁻⁸ , K ₅ = 0.165								
4	0.50	0.10	0.770	0.438	0.038	0.062	3.72	9.76
5	0.95	0.10	0.818	0.872	0.022	0.078	2.74	12.60
6	0.50	0.25	0.777	0.358	0.108	0.142	5.10	11.19
50°, K ₃ = 3.148 × 10 ⁻¹⁵ , K ₄ = 1.968 × 10 ⁻⁷ , K ₅ = 0.115								
7	0.198	0.05	0.775	0.174	0.026	0.024	14.06	26.93
8	0.494	0.05	0.769	0.458	0.014	0.036	9.75	33.90
9	0.198	0.125	0.771	0.145	0.072	0.053	14.93	25.96

^a These nine experiments were run as a continuous series (none discarded!) immediately after the final method had been developed on the basis of 61 preliminary experiments. Calculated values of (I⁻) range from 0.585 × 10⁻¹⁰ in no. 5 to 11.50 × 10⁻¹⁰ in no. 9. See eq 14 and 6.

Kinetic Results.—The results in Figure 1 are typical. The final results are summarized in Table I. The figure and the table support these statements, already made or implied: (1) anomalous initial formation of iodine is eliminated by the use of AgNO₃ as prescribed; (2) the final experimental method gives the highest specific rates, and there is no clear dependence of these specific rates on the absolute rates; (3) although neither k_2 nor k_2' is constant throughout, k_2' has the advantage of including the unavoidable correction for the effect of equilibrium 5 on equilibrium 3.

Mean specific rates by both preliminary and final methods are summarized in Figure 2. Here the k_2'

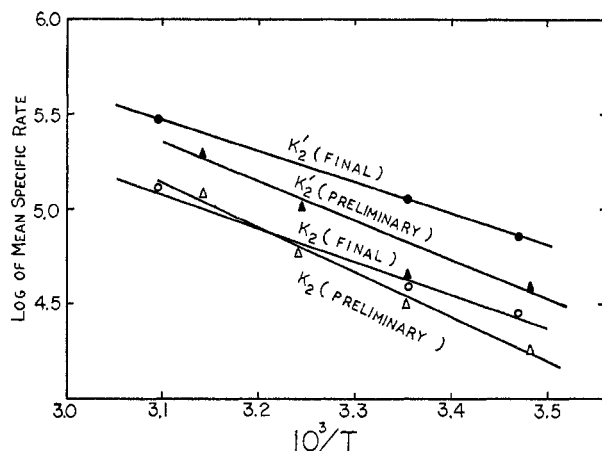


Figure 2.—Specific rates at different temperatures.

final values have a clear advantage. For the final data, the equations of the lines are

$$\log k_2 = -(1.783 \times 10^3/T) + 10.605 \quad (18)$$

$$\log k_2' = -(1.628 \times 10^3/T) + 10.504 \quad (19)$$

and the corresponding heats of activation are -8.16 kcal for k_2 and -7.45 kcal for k_2' .

Discussion of Results.—Figure 2 shows that k_2' , which is defined by

$$\frac{1}{2}d[I_2]/dt = -d[IO_3^-]/dt = k_2'[IO_3^-](I^-)[H^+]^2 \quad (2a)$$

is adequate for calculating the rates of the Dushman reaction at low (I⁻) and at different temperatures.

The principal objective of this investigation has thus been accomplished.

In the usual kinetic studies, reactants at concentrations near 10⁻¹⁰ M either exist as reactive intermediates to which the Bodenstein steady-state approximation is applied or are supplied by a reaction near equilibrium in the phase within which reaction is occurring (e.g., OH⁻ supplied by the dissociation of H₂O). Here iodide must be maintained at a constant concentration by the dissolution of a solid in near-equilibrium with its ions and by three equilibria. Furthermore, the ratio of the rate of reaction to this minute constant concentration is unusually high, being about 3.8 × 10³ in a typical experiment (no. 5, Table I).

Our final experimental method seems trustworthy even though k_2' is not entirely constant. The method gives rates that are constant within the experimental error from $t = 0$, and it gives the highest values of k_2' found in this investigation. The nature of the reaction system suggests that these are two reliable criteria of trustworthiness.

Myers and Kennedy¹¹ and Connick and Hugus¹² have arrived at rate laws for the Dushman reaction by studying the rate of exchange of radioactive iodine between I₂ and IO₃⁻. The simplest and most convincing way to compare the new results with the earlier work is to use the older rate laws to calculate rates for comparison with the rates we measured at 25°. See Table II.

TABLE II
COMPARISON OF RATES MEASURED AT 25° WITH CORRESPONDING CALCULATED RATES

No.	Measd	Rates, 10 ⁷ × mol of IO ₃ ⁻ /(l. min)				Sum
		Abel and Hilferding ^a	Connick and Hugus ^b	Myers and Kennedy ^c First term	Myers and Kennedy ^c Second term	
4	2.50	1.22	3.62	8.83	2.24	11.07
5	6.65	4.39	9.46	19.47	16.15	35.62
6	21.40	7.60	15.81	116.2	10.40	126.6

^a Abel and Hilferding:² rate = 1.84 × 10⁴[I⁻][IO₃⁻][H⁺]².
^b Connick and Hugus:¹² rate = 1.1 × 10⁶(I⁻)(IO₃⁻)(H⁺)³.
^c Myers and Kennedy:¹¹ rate = 3.42 × 10³(γ_{\pm})⁶(I⁻)(IO₃⁻)²(H⁺)³ + 6.6 × 10⁶(γ_{\pm})⁶(I⁻)(IO₃⁻)(ClO₄⁻)(H⁺)³. Time in minutes.

Thermodynamic data used were those in this paper. For this reason, 1.84 × 10⁴ appears in place of 2.47 × 10⁴ in ref 2. The value of the calculated rate is unaffected by the change.

In spite of some large discrepancies, which we cannot explain, we believe that all of Table II deals with the same reaction. We consider the results in the second column to be low mainly because iodide was below its equilibrium concentration. The results in the first column are near those in the third and fifth but below those in the fourth and sixth. The high order of the reaction, its low rate, the minute iodide concentrations, and the thermodynamic complexity of the reaction system—all these—make it difficult (as Table II bears witness) to be sure of the rate law for the Dushman reaction at low iodide concentration.

Finally, is the Dushman reaction of possible significance in the oscillating decomposition of hydrogen peroxide, which occurs after an induction period in the

(11) O. E. Myers and J. W. Kennedy, *J. Amer. Chem. Soc.*, **72**, 897 (1950).

(12) R. E. Connick and Z. Z. Hugus, Jr., Brookhaven Conference Report BNL-C-8, Chemical Conference No. 2, 1948, p 164.

presence of H^+ and IO_3^- at suitable concentrations? It has long been clear that the reduction of IO_3^- by H_2O_2 to give iodine¹³ begins this induction period and continues throughout the decomposition, whether oscillating or smooth.

The oscillating decomposition is characterized by a pulsating evolution of oxygen, for which a peak rate near 1.6×10^{-2} mol/(l. min) has been measured.¹⁴ So long as $[H_2O_2]$ is appreciable, this peak rate is many times the rate of the Dushman reaction calculated from eq 2a for the concentration existing in the H_2O_2 system. But, the latter rate is comparable with the rate of iodine formation that can result from the reduction of IO_3^- by H_2O_2 . For this reduction at 50° , the rate law is¹³

$$+d[I_2]/dt = -\frac{1}{2}d[IO_3^-]/dt = 2.6 \times 10^{-4}[IO_3^-][H_2O_2] + 129 \times 10^{-4}[H^+][IO_3^-][H_2O_2] \quad (20)$$

(13) H. A. Liebhafsky, *J. Amer. Chem. Soc.*, **53**, 896 (1931).

(14) I. Matsuzaki, R. B. Alexander, and H. A. Liebhafsky, *Anal. Chem.*, **42**, 1690 (1970); note Figure 7.

By equating this rate of iodine formation to that calculated from eq 2a, one obtains the (I^-) at which the two rates are equal. At 50° , the mean k_2' is near 29×10^4 . For $[H_2O_2] = 0.5$, $[IO_3^-] = 0.1$, and $[H^+] = 0.1$, equality exists when (I^-) is near 9×10^{-8} . This is a reasonable value for (I^-) during the oscillating decomposition.¹⁴ The Dushman reaction may well be involved. If that is true, then the Dushman reaction will also oscillate, for it is coupled to the decomposition via (I^-) , which shows pronounced oscillations.¹⁴ We could then have a situation in which an oscillating formation of iodine via the Dushman reaction is superimposed on a steady formation of iodine via the reduction of iodate by hydrogen peroxide. Such a situation could obviously influence the pulsating oxygen evolution.

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The Oxidation of Uranium(IV) by Chromium(VI) and the Induced Oxidation of Iodide Ions^{1a}

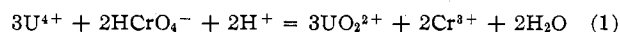
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The oxidation of U(IV) by Cr(VI) proceeds quantitatively to UO_2^{2+} and $Cr(H_2O)_6^{3+}$. A stopped-flow kinetic study was carried out; after allowance for acid dissociation reactions, the rate equation is $-d[Cr(VI)]/dt = \{k' + k[H^+]^{-1}\}[U^{4+}][HCrO_4^-]$, where the acid-independent term, which is quite small, probably represents a medium effect. The reaction produces Cr(V) as an intermediate, as evidenced by the induced oxidation of iodide ions. The iodine yield was evaluated as a function of $[I^-]/[U^{4+}]$ and $[H^+]$ and indicates U(V) is not an intermediate, which is also supported by the effect of Fe^{3+} as well as by ^{18}O studies in the literature. Some experiments on the reactions of U(III) and U(V) with Cr(VI) are also reported.

Introduction

The oxidation of U(IV) by Cr(VI), eq 1, constitutes



a standard volumetric analysis for uranium.² Rao, *et al.*,³ reported that the oxidation occurs rapidly, any apparent slowness being attributable to a sluggish indicator reaction.

We found no indications that earlier kinetic studies had been made, presumably owing to the high reaction rate. The reaction of U(IV) and Cr(VI) induces the oxidation of iodide ions,^{4,5} but the reported yields of iodine could be rationalized only by an involved sequence of reactions with a particular coincidence of rates.⁶ The oxygen-18 study of Gordon and Taube⁷ disclosed appreciable oxygen transfer from Cr(VI) to UO_2^{2+} .

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3117. (b) Fellow of the Alfred P. Sloan Foundation, 1968–1970.

(2) I. M. Kolthoff and J. J. Lingane, *J. Amer. Chem. Soc.*, **55**, 1871 (1933).

(3) V. P. Rao, B. V. S. R. Murty, and G. G. Rao, *Z. Anal. Chem.*, **147**, 199 (1955).

(4) W. Manchot, *Ber.*, **39**, 1352, 3510 (1906).

(5) R. Luther and T. F. Rutter, *Z. Anorg. Chem.*, **54**, 1 (1907).

(6) F. H. Westheimer, *Chem. Rev.*, **45**, 419 (1949).

(7) G. Gordon and H. Taube, *Inorg. Chem.*, **1**, 69 (1962).

We present here the results of a detailed kinetic study carried out in perchlorate solution, as a function of hydrogen ion concentration and temperature. The induced oxidation of iodide was also studied under the same controlled conditions, with results in good accord with a reasonable reaction mechanism. The roles of possible reaction intermediates, particularly Cr(V) and U(V), were studied, by consideration of the iodide experiments, by studying a possible rate effect of $Fe(III)$, by considering the implications of the ^{18}O experiments, and by a direct but cursory examination of the U(V)–Cr(VI) reaction.

Experimental Section

Materials.—Uranyl(VI) perchlorate was prepared by heating U_3O_8 in perchloric acid and crystallizing $UO_2(ClO_4)_2 \cdot XH_2O$. Reduction of the acidified aqueous solutions to U(IV) was accomplished with amalgamated zinc, followed by air oxidation of any U(III) produced. The U(IV) solutions were analyzed by cerium(IV) titration and/or by spectrophotometry.

Solutions of U(V) were prepared by the reaction of europium(II) with uranium(VI) at low acidity.⁸ Other reagents were prepared as before.^{9a,10}

(8) T. W. Newton and F. B. Baker, *ibid.*, **4**, 1166 (1965).

(9) (a) J. H. Espenson, *J. Amer. Chem. Soc.*, **86**, 5101 (1964). (b) As pointed out to the authors by T. W. Newton the left-hand side of eq 24 is equivalent to the simpler expression $(F^{-1} + 1)/3$.

(10) J. H. Espenson and R. J. Kinney, *Inorg. Chem.*, **10**, 376 (1971).