noted that steady state is reached in 10^{-5} and and 10^{-9} second for an initial concentration of bromine atoms equal to zero and $\sqrt{k_1\mathrm{Br}_2/k_5'}$, respectively.

Summary

The rate equations for a coupled set of first order reactions are integrated by a method similar to that used in the determination of the normal coördinates of vibration of molecules.

The equations for the H_2–Br_2 reaction are integrated approximately. The steady condition for H atoms and Br atoms is predicted as well as their respective steady state concentrations.

AUSTIN, TEXAS
BAYTOWN, TEXAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Some Chemical and Physical Properties of Uranium Peroxide

BY GEORGE W. WATT, SIEGRIED L. ACHORN AND JACK L. MARLEY

In the course of certain studies in progress in these laboratories we have accumulated considerable data relative to the solid product that results from the action of hydrogen peroxide upon aqueous solutions of uranyl salts and which has been designated as a peroxyhydrate of uranium (VI) oxide,[1] as peruranic acid,[2] but more commonly as uranium peroxide.[3–7] Since further studies on this product are not planned, it seems worthwhile to record certain of the experimental data which we have obtained. The present studies are concerned primarily with conditions favorable to complete precipitation of uranium as a peroxide, and with the nature of the reaction between uranium peroxide and sulfites.

Experimental

Materials.—All of the chemicals used in this work were reagent grade. The uranium salts taken as starting materials consisted of uranyl nitrate 6-hydrate (Baker and Adamson) and the 2-hydrate prepared by drying the 6-hydrate *in vacuo* over concentrated sulfuric acid.

Anal. Calcd. for $UO_2(NO_3)_2{\cdot}6H_2O$: U, 47.4. Found: U, 47.6. Calcd. for $UO_2(NO_3)_2{\cdot}2H_2O$: U, 55.4. Found: U, 55.3.

Preparation of Uranium Peroxide 2-Hydrate.—A solution (100 ml.) which was 0.1 *M* in uranyl nitrate and 0.1 *M* in nitric acid was heated to *ca.* 90°, stirred, and treated dropwise with 15 ml. of 10% hydrogen peroxide solution (*i. e.*, a quantity insufficient to precipitate all of the uranium as the peroxide). The resulting light yellow precipitate (hereafter designated product A) was digested for one hour at 90°, centrifuged, and washed free of nitrate ion with distilled water. Although different conditions of drying were employed (*e. g.*, air-drying, drying over calcium chloride at atmospheric pressure, drying *in vacuo* over concentrated sulfuric acid, and drying in an oven at 110°), the final product in all cases was the 2-hydrate. All attempts to effect further dehydration at more elevated temperatures led to partial or complete conversion to uranium(VI) oxide.

Anal. Calcd. for $UO_4{\cdot}2H_2O$: U, 70.4; peroxidic oxygen, 9.4. Found: U, 69.8; peroxidic oxygen,[8] 9.3.

Uranium peroxide 2-hydrate was also formed by adding, with stirring, 25 ml. of 0.1 *M* uranyl nitrate solution to an excess (20 ml.) of 10% hydrogen peroxide solution previously made 0.1 *M* in nitric acid and warmed to 40–50°. This precipitate (product B) was subsequently treated as described above except that it was digested at room temperature. It appeared to be less dense and somewhat more intensely colored than product A.

Anal. Calcd. for $UO_4{\cdot}2H_2O$: U, 70.4; peroxidic oxygen, 9.4. Found: U, 70.5; peroxidic oxygen, 9.0.

In view of the apparent difference between the product formed with uranium in excess and that produced with hydrogen peroxide in excess, electron projection and diffraction patterns were obtained[9] using an RCA Type EMU-1 electron microscope and standard techniques of mounting and recording.[10] The diffraction patterns establish the identity of the uranium–uranium distance in the crystals of the two products, and this suggests that the differences readily apparent in the projection patterns (product A: distinct cubes; product B: largely clusters of fine needle-like crystals) reflect only a difference in crystal habit. From numerous projection patterns, it appears that the clusters of crystals present in product B are in no case obtained exclusively and it is therefore not known whether they contribute to the diffraction process.

TABLE I

ELECTRON DIFFRACTION MAXIMA FOR URANIUM PEROXIDE

Product A		Product B	
d, Å.	Rel. intensity	*d*, Å.	Rel. intensity
5.13	Strong	5.21	Strong
4.29	Weak	4.29	Weak
3.84	Medium	3.84	Medium
3.47	Strong	3.47	Strong
3.20	Medium	3.20	Medium
2.64	Weak	2.66	Weak
2.42	Weak	2.36	Weak
2.07	Medium	2.07	Medium
1.92	Strong	1.93	Strong
1.74	Weak	1.75	Weak
1.63	Weak	1.62	Weak
1.48	Weak	1.48	Weak
1.34	Weak	1.34	Weak

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(1) Hüttig and Schröeder, *Z. anorg. allgem. Chem.*, **121**, 243 (1922).

(2) Sievert and Müller, *ibid.*, **173**, 297 (1928).

(3) Fairley, *J. Chem. Soc.*, **31**, 127 (1877).

(4) Alibegoff, *Ann.*, **233**, 117 (1886).

(5) Melikoff and Pissarjewsky, *Z. anorg. allgem. Chem.*, **18**, 59 (1898).

(6) Pissarjewsky, *J. Russ. Phys.-Chem. Soc.*, **35**, 42 (1903).

(7) Rosenheim and Daehr, *Z. anorg. allgem. Chem.*, **181**, 177 (1929).

(8) Determined by titration with standard potassium permanganate solution following acidification with dilute sulfuric acid.

(9) The assistance of Mr. L. L. Antes is gratefully acknowledged.

(10) Zworykin, *et al.*, "Electron Optics and the Electron Microscope," John Wiley and Sons, Inc., New York, N. Y., 1945.

From the projection patterns it is estimated that the particle diameter for product A is 800–1000 Å.; for product B, 200–400 Å. The interplanar spacings and the relative intensities are given in Table I.

Preparation of Uranium Peroxide 2-Hydrate at Controlled *p*H.—At the suggestion of Dr. R. D. Baker, who has carried out similar studies,[11] uranium peroxide 2-hydrate was precipitated under conditions such that *p*H was held substantially constant during the course of the reaction. In a typical experiment, 20.09 g. of uranyl nitrate 6-hydrate was dissolved in 100 ml. of distilled water, stirred vigorously, and treated dropwise with 14% aqueous ammonia to adjust the *p*H to 2.5. The localized precipitate (presumably ammonium diuranate[12]) which formed upon each addition of ammonia redissolved readily. Thereafter, precipitation was effected by addition of an excess of 30% hydrogen peroxide solution while addition of aqueous ammonia was continued at a rate such that the *p*H of the reaction mixture was maintained at 2.5. The precipitate was filtered, washed with distilled water, and dried at 110°. Data relative to this product are given in Table II, which includes similar data for products prepared at *p*H 3.5 and (initially) 4.5. In the latter case, adjustment of the *p*H to 4.5 resulted in a permanent orange-colored precipitate. If this consisted of ammonium diuranate, the data of Table II show that it was converted largely to uranium peroxide upon addition of 30% hydrogen peroxide, because the nitrogen content of the final product limits the ammonium diuranate content to about 5%. The final product was orange-colored rather than pale yellow, and the final *p*H of the reaction mixture was 6.1.

Table II

Precipitation of Uranium Peroxide 2-Hydrate at Controlled *p*H

*p*H	U pptd., %	U, %	N, %
2.5	99.8	69.9	0
3.5	99.9	69.9	0
4.5–6.1	99.8	71.0	0.3

X-Ray (Cu Kα) diffraction data for the products formed at *p*H 2.5, 3.5, 4.5–6.1,[13] and that formed at *p*H ≦ 1 are given in Table III. These data show that the products formed at *p*H 2.5 and 3.5 are identical; reproducibility of analytical data supports the conclusion that uranium peroxide 2-hydrate is the only solid product obtained under these conditions. This same substance is present in the product formed at *p*H ≦ 1, together with one or more other unidentified crystalline solids to which the spacings *d* = 3.23, 2.09 and 1.74 must be attributed. For the product formed at *p*H = 4.5–6.1, the spacings *d* = 5.22 and 3.79 (as well as those corresponding to several less intense lines not indexed in Table III) are attributable to uranium peroxide 2-hydrate, while *d* = 3.17 and 3.52 correspond to the two most intense lines in the diffraction pattern for ammonium diuranate.[14] The spacings *d* = 5.70, 3.91 and 5.65 indicate the presence of at least one additional crystalline component.

Table III

X-Ray Diffraction Data on Products Containing Uranium Peroxide

*p*H ≦ 1		*p*H = 2.5		*p*H = 3.5		*p*H = 4.5–6.1	
d	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
5.19	1.00	5.20	1.00	5.20	1.00	3.52	1.00
3.23	0.38	3.52	0.60	3.51	0.55	3.79	0.74
2.62	.36	3.79	.61	3.77	.51	3.17	.63
4.40	.31	4.38	.36	4.38	.39	5.70	.55
2.09	.24	1.94	.37	1.95	.32	3.91	.55
1.74	.17	2.79	.36	2.74	.32	5.22	.53
1.92	.16	2.66	.31	2.65	.31	5.65	.51

The Reaction between Uranium Peroxide and Sulfites.—Preliminary qualitative experiments showed that uranium peroxide suspended in water is dissolved upon addition of alkali metal or ammonium sulfites *without gas evolution* to form intensely yellow colored solutions. Similar results are obtained when such suspensions are saturated with sulfur dioxide gas, but the solid is not dissolved by treatment with other salts such as nitrites, sulfates and acetates. When relatively large quantities of the solid are treated with small volumes of concentrated solutions of sulfites, the reaction products consist of the yellow solution and a similarly colored crystalline solid.

Proof that the reaction between the peroxide and sulfites results in the formation of uranyl ion and sulfate ion, and that the intensely yellow colored component of the resulting solutions is due to the presence of uranyl and sulfite ions, was obtained as follows. Solutions were prepared by dissolving in 30% ammonium sulfite solution quantities of uranium peroxide and uranyl nitrate such that the final uranium concentrations in the yellow solutions were the same. The absorption spectra of these two solutions over the range 400–700 mμ proved to be substantially the same.[15] In another series of experiments, a 0.001 *M* solution of uranyl nitrate in boiled distilled water was saturated with sulfur dioxide at room temperature. At the same time, a suspension of uranium peroxide was treated similarly using a quantity of the solid such that the final uranium concentrations of the two solutions were the same. The yellow solution formed using the nitrate gave a negative test for sulfate ion while that obtained using the peroxide gave a strong positive test for sulfate ion, and the transmittance of this solution was found to be 68% (as measured with a model 400-A Lumetron and a Corning no. 420 filter). This solution was oxidized by bubbling molecular oxygen through it for five hours, and the transmittance of the resulting solution was found to be 87%. This latter value is identical with the measured transmittance of a solution of uranyl sulfate at the same concentration.[16]

The identity of the soluble product responsible for the intense yellow color of the solution was established spectrophotometrically by the use of Job's method of continuous variations.[17] For these measurements, 0.01 *M* solutions of ammonium sulfite and uranyl nitrate were employed; the nitrate was used rather than the peroxide since one thereby avoids the presence of sulfate ion, and because both nitrate and peroxide yield the same soluble colored product. The absorption spectra obtained using a General Electric automatic recording spectrophotometer are shown in Fig. 1, where curves A to L correspond to solutions in which the ratio $UO_2^{++}/UO_2^{++} + SO_3^{=}$ was varied from unity to zero. In Fig. 2, this concentration ratio is plotted *versus* corrected optical density[18] and shows one maximum in optical density corresponding to $UO_2^{++}/UO_2^{++} + SO_3^{=} = 0.45$. This corresponds rather closely to a 1:1 ratio of uranyl to sulfite ion and this together with the shape of the curve leads to the conclusion that the colored component of the solution is uranyl sulfite which is appreciably dissociated at the concentration of the solutions used in this work.

Several attempts were made to identify the yellow solid formed when uranium peroxide was treated with 30% ammonium sulfite solution, or when 0.2 *M* uranyl nitrate solution was treated with 0.2 *M* ammonium sulfite. Analysis of the intensely yellow solid products showed

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[11] Baker, private communication.

[12] Carson and Norton, *Am. Chem. J.*, **10**, 219 (1888).

[13] The equipment used in this work was made available through the courtesy of Prof. R. F. Shurtz and the measurements were made by Mr. G. L. Sutherland. Their assistance is gratefully acknowledged.

[14] Watt, Jenkins and McCuiston, This Journal, **72**, 2260 (1950).

[15] Achorn, M.A. Thesis, The University of Texas, June, 1948.

[16] Marley, M.A. Thesis, The University of Texas, August, 1949.

[17] Job, *Ann. Chem.*, **9**, 113 (1928).

[18] Foley and Anderson, This Journal, 70, 1195 (1948).

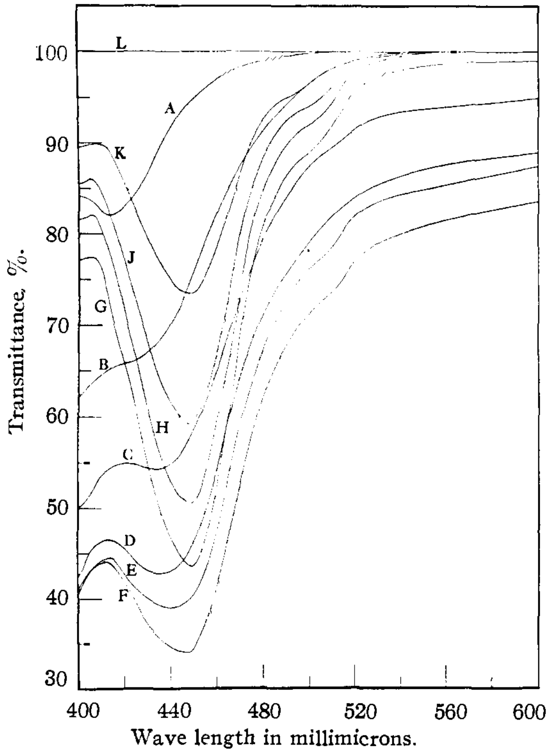

Fig. 1.—Method of continuous variations: solutions containing UO_2^{++} and $SO_3^{=}$.

that the ratio of uranium to sulfite ion varies from approximately 3:2 to 4:3; apparently the solid consists of a mixture the composition of which is partially dependent upon the concentration of sulfite used. This product was not further investigated.

Summary

1. Two different crystalline forms of uranium peroxide 2-hydrate are formed by the reaction between excess uranyl nitrate and hydrogen peroxide, and between uranyl nitrate and excess hydrogen peroxide. The uranium–uranium distance is the same in both types of crystal.

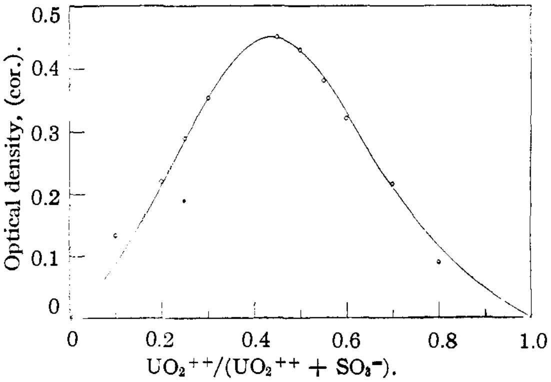

Fig. 2.—Method of continuous variations: λ = 448.

2. The precipitation of uranium as the peroxide 2-hydrate is substantially quantitative at *p*H 2.5 and 3.5. The product obtained at an initial *p*H of 4.5 (following addition of ammonium hydroxide) consists of uranium peroxide 2-hydrate, ammonium diuranate, and at least one other crystalline solid. At *p*H $\leq$ 1, uranium peroxide 2-hydrate and at least one additional crystalline product are formed.

3. Uranium peroxide 2-hydrate is dissolved without gas evolution by aqueous solutions of sulfites to form an intensely yellow solution and (under appropriate conditions of concentration) a similarly colored solid which is apparently a mixture. The soluble product responsible for the color of the solution has been shown to consist of uranyl sulfite, which has not been reported previously.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY]

The System Uranyl Sulfate–Water. II. Temperature–Concentration Relationships Above 250°[1]

BY C. H. SECOY

In the first paper of this series,[2] temperature–concentration data for the system uranyl sulfate–water below 250° were presented. This paper describes an extension of this study to the critical temperature of water.

As a point of special interest, it was thought that this work might add information about the behavior of aqueous solutions of electrolytes at the critical point concerning which very little experimental information is to be found in the literature. Wuite[3] studied the system sodium sulfate–water and found a rapidly diminishing solubility as the critical temperature of water was approached. He reasoned that the solubility curve of the salt in liquid water would blend smoothly into a solubility curve for the salt in water vapor but presented no experimental evidence of this. The accepted value of the critical temperature of water at that time was 365°, and his analysis of the liquid phase in equilibrium at that temperature

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(1) This document is based on work performed under Contract Number W-7405 eng 26 for the Atomic Energy Project at Oak Ridge National Laboratory. Presented before the Division of Physical and Inorganic Chemistry at the 114th National Meeting of the American Chemical Society, Portland, Oregon, September, 1948.

(2) Secoy, THIS JOURNAL, **70**, 3450 (1948).

(3) Wuite, *Z. physik. Chem.*, **86**, 349 (1914).