[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY]

The Reduction of Uranyl Ion in the Uranyl Oxalate Actinometer

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Introduction

The photolysis of oxalic acid solutions sensitized by uranyl salts has been the subject of many investigations, and has been found to correspond essentially to the reaction

$$H_2C_2O_4 \longrightarrow H_2O + CO + CO_2$$

Büchi[1] found that as long as a five-fold excess of oxalic acid is present, the unimolecular law is closely followed. The early work of Fay[2] in this Laboratory demonstrates that a second reaction, involving the reduction of uranyl ion to the tetravalent state, takes place under certain conditions. Büchi,[1] bearing this work in mind, developed a volumetric method for the determination of the uranous salt in the presence of uranyl ion and oxalic acid, in order to make a suitable correction for this side reaction in his quantum yield determination. His procedure involves an empirical end-point correction, and for this reason cannot be considered as a precision method.

The purpose of this experiment was to determine the conditions governing the relative rates of the two reactions.

Analytical

An important part of the problem was to develop a method for the precise determination of tetravalent uranium in the presence of the other constituents of the solution. The objection to Büchi's[1] procedure of titrating the cold solution with potassium permanganate is that the end-point is not sharp, and that a correction must be made for the amount of oxalic acid oxidized at the same time, as the oxidation of uranous salt by potassium permanganate induces the oxidation of oxalic acid even in cold solutions. Potassium dichromate, either alone or in conjunction with diphenylamine, was found to be unsuitable for the same reason. Apparently, the same difficulty would be encountered with any oxidizing agent. The uranyl ion might be titrated with a titanous salt and the result deducted from the total uranium content, but a slight error in this titration would result in a considerable error in the estimation of traces of uranous salt.

Lundell and his associates[3] mentioned that cupferron could be used to separate the two valence states of uranium, but failed to specify the proper conditions. Preliminary experiments showed that the procedure recommended by Holladay and Cunningham[4] for the separation of vanadium from uranium could be adapted to this determination, provided that the concentration of uranyl ion does not exceed that used in the actinometer solution.

A solution of electrolytically prepared uranous sulfate was found, as a mean of three determinations, to contain 0.0044 g. U^{4+} per cc. When 1 cc. of this solution was added to 10 cc. of actinometer solution brought to the proper acidity (6–8% sulfuric acid, in a volume of 20 cc.), a result of 0.0046 g. U^{4+} was obtained as a mean of three determinations. In the presence of higher concentrations of uranyl salts, however, contamination of the cupferron precipitate becomes serious.

Experimental

(I) Relative Rates of the Reactions.—In order to study the rate of change in uranous salt content as the photolysis progress, samples of the actinometer solution were exposed to full sunlight, a flat Pyrex flask serving as containing vessel. A sufficient amount of ultraviolet light penetrated the glass to decompose practically all of the oxalic acid in three hours. From time to time, duplicate samples were withdrawn from the flask by means of a 10-cc. pipet, exercising due care that no error was introduced by the occlusion of gas bubbles. One of the samples was titrated for oxalic acid, and the other was tested for U^{4+} by means of cupferron. Calculated to a percentage basis, the results are given in Table I and plotted in Fig. 1.

TABLE I

Series 1		Series 2	
% $H_2C_2O_4$ decomposed	% UO_2^{++} reduced	% $H_2C_2O_4$ decomposed	% UO_2^{++} reduced
67.5	1.0	42.5	0.0
77.5	1.0	64.3	0.3
80.8	2.1	69.3	1.8
89.5	10.7	71.0	1.8
		71.2	2.5
		83.0	3.2
		85.8	3.3
		88.0	12.5
		90.5	13.0
		94.0	43.4

The decided change in the slope of the curve when the oxalic acid is about 80% decomposed shows that the rate of reduction of UO_2^{++} increases rapidly when there is just enough oxalic acid remaining to form the compound uranyl oxalate.

The actinometer solution made up as used by Anderson and Robinson[5] and Leighton and

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[1] Büchi, *Z. physik. Chem.*, **111**, 269 (1924).

[2] Fay, *Am. Chem. J.*, **18**, 269 (1896).

[3] Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley and Sons, New York, 1931, p. 80.

[4] Holladay and Cunningham, *Trans. Am. Electrochem. Soc.*, **43**, 329 (1923).

[5] Anderson and Robinson, THIS JOURNAL, **47**, 718 (1925).

Forbes[6] contains free sulfuric acid. Believing that the presence of the strong mineral acid might affect the relative rates of the two reactions, we made up a solution from oxalic acid and uranyl oxalate in the ratio 5:1, and exposed it in the same manner. The decided break in the curve occurs at the same place, *i. e.*, after the oxalate in excess of that required to form uranyl oxalate has been decomposed.

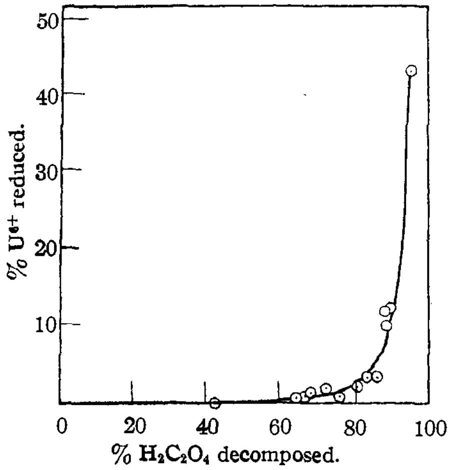

Fig. 1.

(II) Composition of the Photolyte.—Evidently, when excess oxalic acid is present, it inhibits the reduction of UO_2^{++}. The reason for this effect is apparent if we accept the second of two commonly proposed mechanisms for the reaction taking place in the actinometer:

(1) The oxalic acid is decomposed by collisions with activated UO_2^{++}.

(2) The photolyte is a complex. Büchi[1] suggested $H_2C_2O_4 \cdot UO_2C_2O_4$, whereas Leighton and Forbes[6] suggest uranyl oxalate or a "similar optical cluster." Dittrich,[7] however, showed that in a transference cell in the presence of sodium oxalate the uranium migrates to the anode, and a dilute solution of sodium oxalate in contact with excess uranyl oxalate is converted into $Na_2C_2O_4 \cdot UO_2C_2O_4$ when equilibrium is reached. By analogy, one would expect to find, in the actinometer solution, $H_2C_2O_4 \cdot UO_2C_2O_4$, or, more compactly written, $H_2UO_2(C_2O_4)_2$.

The apparent photolysis of the oxalic acid may be attributed to the unimolecular decomposition of the complex acid or its anion, and the reduction of UO_2^{++} to the decomposition of uranyl oxalate molecules in equilibrium with the complex. The concentration of uranyl oxalate, as a simple calculation based upon subsequent data will show, rises from practically zero when the oxalic acid is 60% decomposed (*i. e.*, when there is enough excess oxalic acid to form the complex acid) to 0.01 *M* when the ratio of oxalate to uranium has dropped to unity. It will be observed that the rapid reduction of uranyl ion begins in the vicinity of the latter point, verifying the above deductions.

A method for determining the nature of the complex suggested itself in the course of making certain electrode potential measurements. It was found that the addition of uranyl oxalate markedly increased the acidity of a solution of oxalic acid. This is, of course, contrary to the principle of the common-ion effect by virtue of which the salt of a weak acid represses the ionization of the acid. The increased acidity could not have been caused by the hydrolysis of uranyl oxalate, as a saturated solution of this salt barely affects the color of a solution of methyl orange. The obvious interpretation of this observation was the hypothesis that the complex formed was a stronger acid than oxalic acid, and it seemed desirable to determine the extent of the ionization of the complex. Britton[8] has successfully employed the quinhydrone electrode in his work on the hydrolysis curves of uranyl salts. Preliminary experiments in this laboratory showed that it is also satisfactory in solutions of oxalic acid. Accordingly, an electrode that gave correct readings in a potassium acid phthalate buffer solution, a solution of 0.108 *N* sulfuric acid, and, finally, in 0.108 *N* sulfuric acid also 0.01 *M* with respect to uranyl sulfate,[9] was used in the following experiment.

A solution of 0.01 *M* uranyl oxalate containing also 0.098 *M* oxalic acid was prepared, and 10-cc. samples were agitated with quinhydrone. A solution of 0.01 *M* uranyl oxalate was run in from a buret, the object being to keep the uranium content constant while progressively diminishing the total concentration of oxalate radical. Potentiometer readings were taken, from which the usual calculations are summarized in Table II.

It will be noted that over a fairly wide range the hydrogen-ion concentration furnished by the com-

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(6) Leighton and Forbes, This Journal, **52**, 3139 (1930).

(7) Dittrich, *Z. physik. Chem.*, **29**, 449 (1899).

(8) Britton, *J. Chem. Soc.*, 2467 (1932).

(9) The agreement in *p*H between the two dilute solutions of sulfuric acid was within the limit of accuracy of the potentiometer, showing that this concentration of uranyl salt has no appreciable effect upon the quinhydrone electrode. In a solution of 0.005 *M* sulfuric acid, the discrepancy is no larger than the predictable hydrolysis of uranyl sulfate, the *p*H of which is about 3.5 in 0.01 *M* solutions.

TABLE II

EFFECT OF DILUTING A SOLUTION OF $UO_2C_2O_4$(0.01 *M*) AND $H_2C_2O_4$(0.098 *M*) WITH 0.01 *M* $UO_2C_2O_4$

10-cc. sample taken for each of 3 runs, $T = 23°$, quinhydrone–satd. calomel electrodes

$UO_2C_2O_4$ added, cc.	Ratio $H_2C_2O_4$/ $UO_2C_2O_4$	E. m. f. mean of 3 detns.	$[H^+]$	$[H^+]$ due to complex
0	10	0.3812	0.0600	0.026
5	6.6	.3752	.0472	.022
10	5	.3712	.0405	.022
15	4	.3674	.0348	.020
20	3.3	.3649	.0316	.020
25	2.8	.3625	.0288	.019
30	2.5	.3610	.0270	.019
35	2.2	.3590	.0251	.018
40	2	.3569	.0230	.017
90	1	.3430	.0134	

$$pH = \frac{0.4534 - 0.00009\ (t - 18) - E}{0.0577 + 0.0002\ (t - 18)} = \frac{0.4530 - E}{0.0587}$$

plex is practically constant at 0.02 *M*. Since the complex is 0.01 *M* (assuming that it is the acid corresponding to Dittrich's sodium salt), this corresponds to complete ionization as a dibasic acid. In the three most highly concentrated solutions, the $[H^+]$ is somewhat higher, but these values might be ascribed to a small concentration of $H_6(UO_2)_2(C_2O_4)_5$, the potassium salt[10] of which has been reported. Small amounts of this acid would tend to form in large excesses of oxalic acid, and it would constitute a potential source of hydrogen ion in excess of twice its molality.

On the other hand, when the ratio of oxalic acid to uranyl oxalate has fallen to unity, corresponding to the composition of the complex, the $[H^+]$ has fallen to 0.0134 *M*. This, also, is in conformity with the laws of mass action, from which one would predict that in solutions containing only a slight excess of oxalic acid, a partial dissociation of the complex into its components would take place. The oxalic acid set free would furnish a somewhat smaller contribution to the total $[H^+]$, so that the apparent ionization of the complex would be lowered.

(III) **Stability of the Complex.**—At room temperature, the solubility of uranyl oxalate in pure water was found to be 0.0156 *M*, in substantial agreement with values found in the literature. A freezing point determination showed that it is ionized only to the extent of about 10%, a value close to that found by Dittrich from conductometric measurements.

A solution of approximately 0.05 *M* oxalic acid, after saturation with uranyl oxalate, was found by analysis to contain the following: $[H^+] = 0.0536$ *M*; [Total Oxalate] = 0.0892; [Total U^{VI}] = 0.0357. The term total oxalate comprises, $[H_2C_2O_4]$, $[HC_2O_4^-]$, $[C_2O_4^=]$, $[UO_2C_2O_4]$, and $[H_2UO_2(C_2O_4)_2]$.

Taking the values of the ionization constants of oxalic acid, and Clark's[11] formula

$$\begin{aligned} K_1 &= 3.8 \times 10^{-2} \\ K_2 &= 6.1 \times 10^{-5} \\ &= K/(K + [H^+]) \end{aligned}$$

$[C_2O_4^=]$ is found to be negligible, and the other concentrations:

$$\begin{aligned} [H^+] &= 0.0536\ M \\ [H_2C_2O_4] + [HC_2O_4^-] &= 0.0334 \\ [UO_2C_2O_4] &= 0.0156 \\ [UO_2C_2O_{42}^=] &= 0.0201 \\ \hline \text{Total ionic and molecular species} &= 0.1227 \end{aligned}$$

Here, again, we can calculate the $[H^+]$ furnished by the oxalic acid, *viz.*, 0.0139 *M*, so that the $[H^+]$ furnished by the complex is 0.0397 *M*, or practically twice the molality of the complex.

The corrected freezing-point depression was found to be 0.218°, corresponding to a total molality of ionic and molecular species of 0.117, probably as good a check as could be expected, considering that there was a difference of 23° between the two independent sets of measurements.

Sufficient data are now at hand for the calculation of the equilibrium constant for the reaction

$$UO_2(C_2O_4)_2^= \rightleftarrows UO_2C_2O_4 + C_2O_4^=$$

$$K_i = \frac{[UO_2C_2O_4]\ [C_2O_4^=]}{[UO_2(C_2O_4)_2^=]} = 1.23 \times 10^{-5}$$

Summary

1. An analytical method has been developed for the determination of U^{4+} in the presence of oxalic acid and UO_2^{++}.

2. The change in U^{4+} content with decomposition of oxalic acid during the photolysis of uranium oxalate actinometer solution has been followed.

3. Proof has been offered that in dilute solutions, the composition of the complex undergoing unimolecular decomposition is $UO_2(C_2O_4)_2^=$, and that the source of the U^{4+} is the uranyl oxalate molecule.

4. In dilute solutions, the value for the instability constant of this complex is of the order of magnitude of 1.23×10^{-5}.

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(10) Seidell, "Solubility of Organic and Inorganic Compounds," 2d ed., D. Van Nostrand Co., New York, 1919, p. 735.

(11) Clark, "The Determination of Hydrogen Ions," 3d ed., Williams and Wilkins Co., Baltimore, 1928, p. 14.

5. The ionization of this complex as an extremely strong acid has been discussed.

6. Evidence has been offered as to the existence in concentrated solutions of a substance more complex than $H_2UO_2(C_2O_4)_2$.

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The Atomic Weight of Rubidium

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Somewhat over thirty years ago, one of the authors studied the atomic weight of rubidium through the determination of the silver chloride and bromide equivalents of rubidium chloride and bromide, as well as the silver equivalent of these salts. During the intervening years, several investigators have developed improvements that allow more precise measurements to be made of the quantities involved. In particular the technique of approaching and attaining the exact endpoint of the reaction concerned, has received a lot of attention. With these considerations in mind, it was decided that a new study of the equivalent in question was advisable.

Materials

In the preparation or purification of the chemicals necessary for this investigation, platinum and quartz vessels were used almost exclusively; only when such containers would be attacked did we resort to the use of Pyrex ware.

The water, the several acids, invert sugar, sodium hydroxide, calcium oxide, barium hydroxide, tartaric acid and silver were purified by standard methods.

Iodine Monochloride.—The iodine for this reagent had been sublimed three times, a thorough grinding with potassium iodide preceding the first sublimation. The chlorine was prepared from redistilled hydrochloric acid and potassium permanganate that had been three times recrystallized. The gas was passed over the solid iodine until the mass had been completely liquid for several minutes. The product was then distilled from quartz and came over at a constant boiling point of 101°.

Rubidium Chloride.—The starting material was C. P. rubidium salts, chiefly the carbonate, with small amounts of sulfate and bromide. These were dissolved in water and the solutions filtered. All were then converted to the chloride, and from a warm, saturated solution of this salt the dichloroiodide was precipitated by the addition of the pure iodine monochloride. The rubidium dichloroiodide was then fractionally recrystllaized ten times in quartz vessels, the crystals being drained each time on porcelain in the centrifuge at the usual 1500 r. p. m. As the compound is appreciably soluble in water, even at low temperatures, a second crop of crystals was taken from the mother liquor each time, and there was still a considerable amount of salt left in the residual liquor; but it must be an efficient method of eliminating alkali metals of lower atomic mass.

In making these crystallizations it is very necessary to use water containing about 5% of hydrochloric acid when dissolving the halide salt. Otherwise, decomposition takes place and too much iodine is set free.

The final product of dichloroiodide was converted through the sulfate to the hydroxide by means of the purified barium hydroxide. The pure tartaric acid was then used to convert the rubidium hydroxide to acid tartrate and the acid salt was recrystallized five times with the usual drainage in the centrifuge, in order to eliminate any cesium that might have accumulated during the double halide crystallizations. As the cesium acid tartrate is appreciably more soluble than the rubidium salt, recrystallization should leave the former tartrate in the mother liquor.

The final fraction of acid tartrate was ignited in platinum, and the carbonate obtained treated with pure hydrochloric acid. The chloride solution was diluted and filtered through a Gooch–Munroe crucible. Three crystallizations as chloride followed, the first from hydrochloric acid solution and the last two from water. After the centrifuge draining, the last crop of crystals was dried at 150° and placed in a desiccator over fused potassium hydroxide.

During the treatment outlined above, silica beakers of 250–300 cc. capacity were used for the halide crystallizations, and platinum and silica dishes in the later procedure, whichever were considered the better for the purpose in hand.

That the final product of rubidium chloride was free from the impurities most difficult to get rid of, sodium, potassium, and cesium was indicated by the spectrum photographs; samples examined in the copper arc showed no indications of the lines pertaining to these three metals.

Balance and Weights

The balance used was a No. 10 Troemner with which weighings could be duplicated to 0.02 mg. The weights were corrected according to the method suggested by Richards.[1] Independent comparisons by two observers gave corrections identical within the errors of the experiment. This gave us additional assurance of the constancy of the weights. The weighings were made by substitution using counterpoises of glass and platinum similar to the objects being weighed.

The Analysis of Rubidium Chloride

The analyses were made by the conventional titration method, first devised by Richards and

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(1) Richards, THIS JOURNAL, 22, 144 (1900).