5. The disagreement in this case can hardly be attributed to any uncertainty in the experimental data or in the measured activity coefficients for the pure salts in their saturated aqueous solutions, but probably reflects the limitations of the assumptions embodied in the empirical equation itself.

6. The ternary isotherms obtained for this system have been compared with the binary diagram[7] for the system silver sulfate–sodium sulfate, and a schematic diagram has been drawn for the isotherm of the condensed system.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Behavior of Uranyl Solutions in a Mercury Reductor

BY EARLE R. CALEY[1] AND L. B. ROGERS[2]

McCay and Anderson,[3] McCay,[4] and Furman and Murray[5] have shown that the mercury reductor may be used with advantage in the volumetric determination of antimony, iron, molybdenum or vanadium. These authors say very little about the behavior and possible interference of uranium in such determinations. McCay and Anderson[3] simply state that uranyl ion is not reduced, but one of us (E.R.C.) noticed that this is not true if the solution contains hydrochloric acid in sufficient concentration. Moreover, in contrast to the action of amalgamated zinc the reduction appeared to stop after reaching the quadrivalent stage. Consequently the development of a very convenient method for the determination of uranium seemed possible. Subsequent investigation has now shown that this reduction is never entirely quantitative, though it is so nearly so that accurate results may be obtained by the use of a small correction factor.

Experimental

Apparatus and Solutions.—The reductors were of the type described by McCay.[4] These were charged with distilled mercury. The weights and volumetric ware were carefully calibrated before use.

Potassium dichromate solution, exactly 0.1000 N, prepared from carefully dried salt of high purity, was used as the standard oxidizing reagent. Ferrous sulfate solution, approximately tenth normal, was the reducing reagent. This was always standardized immediately before use, the end-point of this titration, and of the back titrations in experimental runs, being detected by means of a platinum-tungsten pair of electrodes in connection with a vacuum tube voltmeter, as designed by Garman and Droz.[6]

The standard uranium solution, approximately tenth normal, was a uranyl acetate solution acidified with just sufficient acetic acid to prevent spontaneous hydrolysis. This was standardized by precipitating the uranium in measured volumes with carbonate-free ammonium hydroxide reagent, igniting the precipitates to uranium oxide in a muffle furnace at 800°, and weighing. The results of this gravimetric standardization were checked by reducing other measured portions in a Jones reductor according to the procedure of Lundell and Knowles,[7] and then titrating the resulting uranous solution with standard dichromate solution according to the method of Kolthoff and Lingane.[8] The volumetric results checked those obtained gravimetrically within one part per thousand.

General Procedure.—A 25.00-ml. portion of the standard uranium solution was pipetted into a reductor containing 250 g. of mercury. A measured volume of a given acid, usually hydrochloric, was added together with sufficient distilled water to bring the final volume of the water phase to 100 ml. In some experiments certain amounts of sodium chloride were introduced into the system along with the uranium solution. After the air above the liquid had been displaced with carbon dioxide or nitrogen, the reductor was placed in a shaking machine for shaking at a given rate for a given time period. The reduced solution was then transferred to a folded filter with the aid of boiled and cooled distilled water, and the solution thus freed from suspended mercury and mercurous chloride was collected in a measured volume of the standard dichromate solution. The excess of dichromate solution was then determined by back titration with the standardized ferrous sulfate solution, and the degree of reduction calculated.

Results

Effect of Hydrochloric Acid Concentration.—The importance of the concentration of hydrochloric acid is clearly shown by the results in the first two columns of Table I. These results were obtained at room temperature with a fifteen-minute reduction period and a fixed vigorous rate of shaking of the reductor. It will be seen that under these conditions the degree of reduction does not reach a maximum until the concentration of the hydrochloric acid is around 7 N,

TABLE I

EFFECT OF HYDROCHLORIC ACID CONCENTRATION AND TIME ON COMPLETENESS OF REDUCTION

Effect of acid		Effect of time[a]	
Normality of acid	Per cent. reduced	Reaction time, min.	Per cent. reduced
0.96	1.0	5	11.3
2.16	5.2	10	14.9
2.64	10.8	20	31.6
3.00	28.9	45	34.7
3.60	51.0	70	75.5
4.32	98.6	105	94.3
5.28	98.9	305	96.9
6.00	99.1		
7.00	99.3		
8.00	99.4		
9.00	99.3		

[a] In 3.36 N hydrochloric acid.

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[3] McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921); **44**, 1018 (1922).

[4] McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

[5] Furman and Murray, THIS JOURNAL, **58**, 1689 (1936).

[6] Garman and Droz, *Ind. Eng. Chem., Anal. Ed.*, **11**, 398 (1939).

[7] Lundell and Knowles, *Ind. Eng. Chem.*, **16**, 723 (1924).

[8] Kolthoff and Lingane, THIS JOURNAL, **55**, 1871 (1933).

and that higher concentrations of hydrochloric acid produce no appreciable increase. It was found that at concentrations above 6 N the results as to degree of reduction could be reliably reproduced to about one part per thousand. Because of the possibility that the observed incomplete reduction was a fictitious result caused by slight air oxidation occurring after complete reduction by the mercury, experiments were run in which unusual precautions were taken to exclude oxygen throughout the procedure. These precautions included thorough deaeration of the reductor, and the filtration and handling of the reduced solution in an inert atmosphere. These precautions only increased the observed degree of reduction to 99.6% as a maximum. Likewise a considerable increase in time of reduction did not improve the results. It was finally concluded, therefore, that the reduction of uranyl solutions with mercury is never entirely complete even when they contain hydrochloric acid in very high concentration. The degree of incompleteness of reduction varies from 4 to 7 parts per thousand depending upon the exact conditions of experiment and manipulation. In spite of this incompleteness of reduction, the mercury reductor may, nevertheless be used for obtaining satisfactory quantitative results in the determination of uranium since a positive correction of 5 parts per thousand applied to titration figures yields final results equal in accuracy to those ordinarily obtained in the determination of this element.

In connection with such possible analytical application of the reduction of uranyl solutions with mercury, experiments were also run to determine the ease of air oxidation of uranous solutions containing very high concentrations of hydrochloric acid. For example, when a reduced solution was allowed to stand in an open beaker for forty-five minutes before titration the results were 3 parts per thousand below those obtained in the usual way. A similar result was obtained by bubbling a brisk current of air for ten minutes through a reduced solution contained in a beaker. Evidently uranous solutions containing high concentrations of hydrochloric acid are not readily oxidized by contact with air. The amount of exposure necessary in an ordinary analytical procedure should not introduce an appreciable error. It may be that the slight amount of oxidation observed in these experiments really represents oxidation of trivalent uranium, though no other indication of over-reduction with mercury was obtained in the course of this investigation.

Various Factors Influencing Reduction in Hydrochloric Acid Solutions.—In very high concentrations of hydrochloric acid, 6 N or more, the time required to reach a maximum degree of reduction was found to be very short, too short for any reliable measurement of rate by the method of the present experiments. On the other hand, with concentrations under 2 N the time required to reach a maximum was very long, but since the total amount of reduction was small the increments as measured at different time intervals were themselves very small. In intermediate concentrations of acid the degree of reduction was found to vary greatly with time. This is shown by the illustrative results in the last two columns of Table I. Such results were not found easy to duplicate closely because of the great dependence of the rate of reduction not only on time but on variations in amount of contact with freshly exposed mercury surfaces, in other words, on variations in the degree of shaking and in contact during the operations of filtering and washing.

Temperature also considerably influences the rate of this reduction, at least in the intermediate range of acid concentration where measurement can conveniently be made. For example, in parallel experiments with 3.36 N acid, when shaking was done at the same fixed rate for a fifteen-minute period, the average degree of reduction reached at 25° was found to be 30.0%, whereas at 55° it was found to be 66.0%.

However, these various factors are of little significance for the practical analytical application of this reduction to the amounts of uranium usually encountered in macro analysis since with the proper concentration of hydrochloric acid the reduction occurs to the maximum possible extent in a few minutes regardless of considerable variations in rate of shaking and temperature. Experiments on variations in the concentration of the uranium solution also indicated that within the range likely to be encountered in analytical work concentration has no significant influence on the degree of reduction.

Action of Other Acids and of Chloride.—In view of the usually pronounced effect of changes in acidity on oxidation–reduction potentials it might reasonably be expected that the pronounced effects of a high concentration of hydrochloric acid on the reduction of uranyl solutions with mercury is merely a consequence of high hydronium ion concentration. However, very little reduction was found to occur in sulfuric acid solutions of equivalent concentration. In 18 N sulfuric acid, for example, the degree of reduction barely exceeded 1%. In solutions of low acidity, chloride ion did not cause a pronounced degree of reduction. For instance, in a uranyl acetate solution to which sufficient sodium chloride has been added to cause the formation of a visible amount of mercurous chloride in the reductor the degree of reduction was a little under 2%. Evidently, the simultaneous presence of both hydronium ion and of chloride in high concentration is necessary.

Discussion.—According to the experiments of Luther and Michie[9] the E_0 potential of the uranous–uranyl system in acid solution is roughly

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[9] Luther and Michie, *Z. Elektrochem.*, **14**, 826 (1908).

−0.42 volt, and Latimer[10] has calculated it to be approximately −0.33 volt. According to Furman and Murray[5] the E_0 potential of the mercury–mercurous system in hydrochloric acid solution varies from about −0.4 volt in solutions of very low acidity to about 0.0 volt in solutions 9 N in this acid. These data account satisfactorily in a qualitative way for the experimental observations reported in the present paper. The E_0 potential of the uranous–uranyl system is so close to that of the mercury–mercurous system in solutions of very low acidity that only partial reduction to uranous ion can occur. With increase in concentration of acid the E_0 potential of the mercury-mercurous system finally rises so far above that of the uranous–uranyl system that reduction can become essentially complete. Moreover, by analogy with other corresponding systems it is very likely that the E_0 potentials of the uranous–uranyl system actually falls considerably with increasing acidity so that the difference between the E_0 potential of the two systems at high hydrochloric acid concentrations would be greater than the above data indicate. A rigorous treatment of the mutual relationships of the two systems considered here must await more precise measurements, particularly of the uranous–uranyl system.

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Summary

1. In solutions containing hydrochloric acid in sufficiently high concentration, uranyl ion is almost quantitatively reduced to uranous ion in the mercury reductor.

2. The simultaneous presence of both hydronium ion and chloride ion in high concentration is necessary. This may be explained from the E_0 potentials of the uranous–uranyl and the mercury–mercurous systems.

3. By the use of a small correction factor this reduction may be applied to the volumetric determination of uranium. The possible interference of uranium should be taken into account when using the mercury reductor for the determination of certain other elements.

PRINCETON, NEW JERSEY RECEIVED JUNE 10,1946

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(10) Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, p. 239.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA]

Electron Deficient Molecules. II. Aluminum Alkyls

BY KENNETH S. PITZER AND HERBERT S. GUTOWSKY[1]

In the first paper[1a] of this series, the most extensive series of electron deficient molecules, the boron hydrides, were considered and the concept of a protonated double bond advanced to account for their peculiar formulas. Aluminum trimethyl and triethyl[2] have also been reported to be anomalous in that they are dimeric under suitable conditions. We have prepared the methyl, ethyl, n-propyl, and i-propyl aluminum compounds and find all but the last to be dimeric under some conditions. Various data were obtained concerning these substances in the hope of elucidating the cause of their dimerization.

Experimental

Preparation of Compounds.—A very convenient method was developed for the preparation of aluminum trimethyl, based on the type of reaction described by Grosse and Mavity.[3] A distilling column of ten to twenty theoretical plate efficiency is fitted for use with an atmosphere of nitrogen either at 1 atm. or reduced pressure. Methyl iodide is placed with an excess of granular aluminum in the still pot and is mildly refluxed under 1 atm. of nitrogen for twelve or more hours until all methyl iodide has reacted. The temperature is then raised and the pressure reduced to about 10 cm. By maintaining a high reflux ratio, pure $Al_2(CH_3)_6$ may be taken off up to about 50% of the theoretical yield based on methyl groups. No doubt this yield could be increased by the use of greater fractionating power but this was not important for our purposes.

The initial reaction produces a general mixture of aluminum methyl iodides from which the most volatile, aluminum trimethyl, can be distilled. However, considerable fractionating power and a very slow take off are necessary so that the various rearrangement reactions may proceed. This preparation is far simpler for laboratory purposes than any previously used.

Unfortunately, the decreasing volatility of the higher alkyls prevented this new procedure from succeeding, even with the triethylaluminum. These compounds were prepared from the mercury alkyls.

Mercury ethyl, n-propyl and i-propyl were prepared without difficulty according to the method of Gilman and Brown[4]

$$2RMgX + Hg_2Cl_2 = HgR_2 + 2MgXCl$$

The mercury alkyls then reacted with aluminum in a bomb tube at 110° for about thirty hours. Aluminum ethyl and n-propyl were obtained in good yield. With the i-propyl compound a great deal of difficulty arose, presumably because of the instability of mercury i-propyl. In the only successful reaction the bomb tube was held at 60–70° for

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(1a) K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

(2) A. W. Laubengayer and W. F. Gilliam, *ibid.*, **63**, 477 (1941), who give references to earlier work. Professor Laubengayer in a private communication also states he has found these compounds to be dimeric in benzene solution.

(3) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 106 (1940).

(4) H. Gilman and R. E. Brown, THIS JOURNAL, **52**, 3314 (1930).