binations above 1250 cm.$^{-1}$. The present data (summarized in Table II) are in good agreement with ref. 11, except for the $\nu_1(a')$ fundamental for C_2Cl_3D. The present value is considered reliable to ±2 cm.$^{-1}$ and is identical with the Raman value.[12]

Acknowledgment.—The authors appreciate the financial support of the Atomic Energy Commission and the Michigan Memorial–Phoenix Project.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

The Behavior of Uranyl and Neptunyl Ions with Dowex-50 Cation-exchange Resin[1]

BY J. C. SULLIVAN, DONALD COHEN AND J. C. HINDMAN

RECEIVED JULY 5, 1955

During the course of an investigation of the kinetics of an oxidation–reduction reaction in a mixed sulfuric acid–perchloric acid media it became desirable to attempt to ascertain the degree of association between Np(VI) and bisulfate ion. The distribution of a metal ion between an aqueous phase and a solid phase composed of a synthetic cation exchanger has been demonstrated to yield quantitative data on the composition of complex ion systems.[2]

In order to demonstrate that the method was indeed applicable under the conditions of this investigation it was deemed advisable to first determine the association constant for some system that had been previously studied by other means. Accordingly we have determined the complexity constants for uranyl sulfate.

Experimental

The ion exchanger used in this study was Analytical Grade AG 50-X12 processed from Dowex-50 by Bio Rad Laboratories. The hydrogen form of the resin was 200–400 mesh. In addition to the intensive purification by the processor the resin was treated with molar perchloric acid followed by exhaustive water washes. The resin was then oven dried at 80° for three hours.

The U^{233} was purified by an ether extraction just prior to use. The Np^{237} was from a pure stock and the oxidation states prepared as previously described.[3]

Known masses of the resin (usually about 0.2 g.) were introduced into 10-ml. erlenmeyer flasks. Measured volumes of solution containing the metal ions in concentrations of the order of magnitude 10^{-4}–10^{-6} molar were then introduced into the flasks which were then agitated in a constant temperature water-bath for timed intervals.

After equilibration the phases were separated. Aliquots of the aqueous phase mounted on tantalum plates were assayed using a methane proportional α-counter.

Results and Discussion

Defining the distribution coefficient in the absence of a complexing agent we have

$$K = [MR]/[M] \qquad (1)$$

where [MR] is the concentration of the metal in the resin phase per gram of air dried resin and [M] is the concentration of the metal ion in solution per ml. of solution at equilibrium. Upon the introduction of a complexing agent (1) becomes

$$K_1 = \frac{[MR]}{[M] + [MA] + \cdots} \qquad (2)$$

Then any of the standard techniques for the calculation of association constants can be employed.[4] This approach ignores the change in composition of the solution and the resin caused by the exchange reaction as well as assuming constancy of metal ion activities. At the metal ion concentrations used the loading of the resin is negligible. Thus the equilibrium constants are concentration ratios for solutions of the given composition.

Included in Table I are the results of the distribution of uranyl ion between 0.955 M $HClO_4$ and the resin as a function of time. Figure 1 graphically demonstrates the variation of the distribution coefficient as a function of bisulfate concentration at constant ionic strength. The solid line is a theoretical curve with the values of the constants k_1 and k_2 given in the defining equations below

TABLE I

DISTRIBUTION COEFFICIENTS OF UO_2^{+2}, NpO_2^{+2} AND NpO_2^+ BETWEEN DOWEX-50 AND 1 M $HClO_4$ AT 25°, μ = 1.0

Time, min.	K		
	UO_2^{+2}	NpO_2^{+2}	NpO_2^+
60	72.6 ± 1.0	5.43 ± 0.04	5.40 ± 1.3
120	74.6 ± 0.1	8.65 ± .98	8.61 + 0.50
180	74.3 ± 1.3	9.13 ± .11	9.72 ± 1.15
240	74.6 ± 1.4	12.12 ± 1.0	14.03 ± .01

$$\frac{[UO_2SO_4]}{[UO_2^{+2}][HSO_4^-]} = \frac{k_1}{[H^+]} = 6.25 \pm 0.75 \qquad (3)$$

$$\frac{[UO_2(SO_4)_2]^{-2}}{[UO_2SO_4][HSO_4^-]} = \frac{k_2}{[H^+]} = 1.22 \pm 0.30 \qquad (4)$$

Comparison with the previous values for the constants reported by other investigators[5] indicates that the method yields the desired quantitative information.

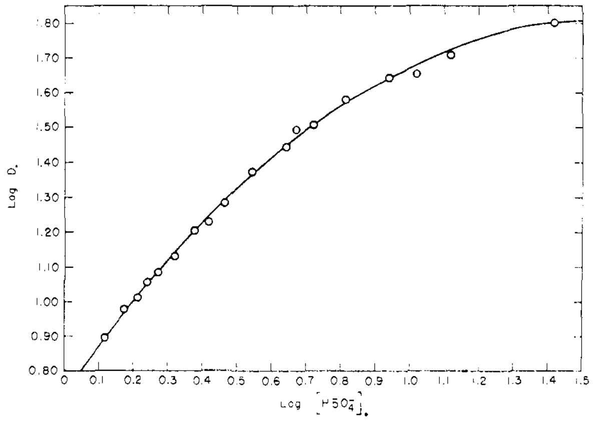

Fig. 1.—Variation of the distribution coefficient of uranyl ion as a function of bisulfate ion at 25.0° and μ = 1.0.

In an effort to extend the technique to a new system the distribution of NpO_2^{+2} between the perchloric acid and the resin was measured as a function of time. The data for this set of experiments are

---

[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] See, for example, S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951).

[3] D. Cohen and J. C. Hindman, THIS JOURNAL, **74**, 4679 (1952).

[4] J. C. Sullivan and J. C. Hindman, *ibid.*, **74**, 6091 (1952).

[5] R. A. Day, Jr., and R. M. Powers, *ibid.*, **76**, 3895 (1954); S. Ahrland, *Acta Chem. Scand.*, **5**, 1151 (1951); R. H. Betts and R. K. Michels, *J. Chem. Soc.*, Supp. Issue #2, S286 (1949).

also included in Table I. The poor precision of the results plus the fact that the value of the distribution coefficient differed so markedly from that for uranyl ion leads to the hypothesis that a reaction other than the exchange is taking place. Despite the fact that Np(VI) is stable in molar perchloric acid with respect to reduction to Np(V) the obvious assumption to make is that the organic substrate, *i.e.*, either the hydrocarbon skeleton of the Dowex-50 and/or the nuclear sulfonic acid which acts as the exchange group, promotes this reduction. This conclusion is supported by the data included in Table I for the distribution of Np(V) between molar perchloric acid and the resin.[6]

The reduction of Np(VI) to Np(V) was then qualitatively demonstrated by equilibrating a solution of 6×10^{-3} M Np(VI) in 0.955 M perchloric acid with about 0.2 g. of the dry resin for a period of one hour. At the end of this time the solution was centrifuged and an absorption spectra of the aqueous layer was taken. The spectra showed the presence of Np(V). Within the experimental uncertainties reduction was complete. The slow increase in the distribution coefficient in the Np(V) solution indicates a further reduction to Np(IV) is occurring.

In the light of these observations the correlation between cation exchange column behavior and the degree of association between Np(VI) and chloride ion[7] is subject to reservations.

---

(6) Qualitative tests for the presence of Cl^- and iron in the wash liquid from the resin were negative. Resin that had been equilibrated for as long as 24 hours with molar perchloric acid showed some evidence of decomposition, namely, a positive test for sulfate in the aqueous phase.

(7) R. M. Diamond, K. Street, Jr., and G. T. Seaborg, THIS JOURNAL, **76**, 1461 (1954).

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Preparation of Palladium(II) Chloride–1,2,3-Benzotriazole Coördination Compounds[1]

BY RAY F. WILSON AND LOUBERTA E. WILSON

RECEIVED JULY 11, 1955

In connection with a general study of the reactions between the platinum elements and 1,2,3-benzotriazole, two palladium coördination compounds have been prepared. 1,2,3-Benzotriazole was first suggested as a precipitant for silver by Remington and Moyer[2] and later by Tarasevich[3] and Cheng.[4] Curtis[5] has employed the same reagent for the determination of copper. These authors report that nickel(II), cobalt(II), iron(II), zinc and cadmium are also precipitated by 1,2,3-benzotriazole; however, a study of the interaction of palladium or other platinum elements with this reagent appears not to have been made previously. The reactions of previously reported ions with 1,2,3-benzotriazole, in contrast to the corresponding palladium reactions, involved the removal of an acidic hydrogen from the reagent. Similar coördination compounds of palladium[6,7] have been reported.

Experimental

Materials.—A weighed amount of palladium(II) chloride, obtained from Coleman and Bell Company, was dissolved in a small amount of concentrated hydrochloric acid and then diluted to volume with distilled water. The resulting solution, which was approximately 0.1 M in hydrochloric acid, was analyzed for palladium content both gravimetrically[8] and polarographically.[9]

Standard 1,2,3-benzotriazole solution in 50% acetic acid was prepared after recrystallizing this reagent, Eastman Kodak Chemical No. 2759, twice from chloroform; the melting point of the recrystallized reagent was 100.0°.

All other materials used were reagent grade chemicals.

Apparatus.—A mechanized, micro-combustion Sargent apparatus was employed for the determination of carbon, hydrogen and palladium.

Procedure.—To four beakers each containing 0.417 mmole of palladium were added 10 ml. of 2 M acetic acid–sodium acetate buffer, and a slight excess of 1,2,3-benzotriazole (dissolved in 50% acetic acid); one palladium ion in excess benzotriazole reacts with two molecules of the reagent. The white colored precipitates were digested for 10 minutes, and then filtered using weighed, medium porosity, sintered-glass crucibles. The precipitates were washed several times with dilute hydrochloric acid (1:100), and finally several times with distilled water. After each precipitate had been dried at 110° for 1 hour to constant weight, the following weights of the four precipitates were obtained: 174.1, 173.0, 173.4, 173.0 mg. *Anal.* Calcd. for the white colored precipitate: C, 34.66; H, 2.42; Cl, 17.06; N, 20.21; Pd, 25.66. Found: C, 34.68; H, 2.45; Cl, 17.05; N, 20.19; Pd, 25.64.

Aliquots of the standard solution of palladium were transferred to three beakers, and 10 ml. of buffer added to each beaker. Then standard 1,2,3-benzotriazole solution was added in amounts such that the molar concentration of palladium remained in slight excess; in each case 0.500 mmole of reagent was added. After standing at room temperature for 12 hours, the precipitates were filtered using fine porosity, sintered-glass crucibles and were washed, dried and weighed in the usual manner. The three reddish-brown precipitates gave the following weights: 148.4, 147.6 and 148.1 mg. *Anal.* Calcd. for the reddish-brown colored precipitate: C, 24.28; H, 1.70; Cl, 23.90; N, 14.16; Pd, 35.96. Found: C, 24.29; H, 1.70; Cl, 23.89; N, 14.14; Pd, 35.96.

Quantitative analysis for nitrogen was carried out using micro Kjeldahl procedure[10] for chlorine by the Carius method[10]; and for carbon, hydrogen and palladium by modifying slightly the procedure described by Steyermark.[10] A Sargent carbon–hydrogen apparatus was employed for the micro-determination of carbon and hydrogen. Following the determination, the carbon dioxide and the water absorption tubes were removed from the apparatus, and the palladium was ignited again in an atmosphere of carbon dioxide to make sure that all the palladium and/or palladium residue had been converted to the metal.

Discussion

Palladium(II) chloride reacts with 1,2,3-benzotriazole to form two different coördination compounds, depending on which is in excess, palladium or 1,2,3-benzotriazole. Both the white and the reddish-brown colored precipitates were very insoluble in most organic solvents and in most concentrated inorganic acids. These precipitates appeared to be sparingly soluble in warm sulfuric acid;

---

(1) This work was supported by a grant from the National Science Foundation.

(2) W. J. Remington and H. V. Moyer, "Dissertation Abstract," Ohio State Univ. Press, Columbus, Ohio, 1937, p. 24.

(3) N. I. Tarasevich, *Vestnik Moskov. Univ.*, **3**, No. 10, 161 (1948).

(4) K. L. Cheng, *Anal. Chem.*, **26**, 1038 (1954).

(5) J. A. Curtis, *Ind. Eng. Chem., Anal. Ed.*, **13**, 349 (1941).

(6) J. H. Yoe and L. G. Overholser, THIS JOURNAL, **61**, 2059 (1939).

(7) J. R. Hayes and G. C. Chandler, *Ind. Eng. Chem., Anal. Ed.*, **14**, 491 (1942).

(8) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 379.

(9) R. F. Wilson and R. C. Daniels, *Anal. Chem.*, **27**, 904 (1955).

(10) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Company, Philadelphia, Pa., 1951, pp. 82–191.