were observed in the polyphosphate complexes of sodium and potassium. The larger effect in the acidic pyrophosphate complex of calcium probably is due to the closer approach of the hydrogen ion in the pyrophosphate complex in contrast to its approach in the triphosphate complex. This effect should be greater in the case of calcium which is already less firmly bound than magnesium.

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COLUMBUS, OHIO

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

Ceric Reduction and the Radiolytic Hydrogen Yield[1]

BY H. A. MAHLMAN

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The hydrogen yields observed in the cobalt-60 γ-ray irradiation of sulfuric acid solutions of ceric ions indicate an acid independence to 0.8 M H_2SO_4. The suppressive action of the solute may be expressed by the equation $G(H_2) = -0.21 [Ce^{IV}]^{1/3} + 0.44$. The scavenging effect of ceric ion indicates that the theoretical cerous yield may be obtained only in infinitely dilute ceric solutions.

The hydrogen yields in cobalt-60 γ-ray irradiation of 0.4 M H_2SO_4 solution and dilute H_2SO_4 solution pH 2 have been generally accepted to be 0.40 and 0.45, respectively.[2] In disagreement it was reported that in 0.4 M H_2SO_4 and 0.5×10^{-3} to 0.5×10^{-6} M H_2SO_4 solutions,[3] containing 10^{-3} M KBr to protect the molecular hydrogen formed from radical attack, the hydrogen yield was the same and equal to 0.45. The presence of HSO_4^- and $SO_4^{=}$ has been shown to have no effect on the hydrogen yield from cobalt-60 irradiated solutions.[4] The purpose of this paper is to present confirmatory evidence that the $G(H_2)$ in a 0.4 M H_2SO_4 solution is 0.45, that this yield is constant to 0.8 M H_2SO_4 and to show that the $G(Ce^{III})$ in an 0.4 M H_2SO_4–Ce^{IV} solution can approach 2.34 only when the concentration of Ce^{IV} approaches zero.

The chemicals were Baker and Adamson C.P. grade sulfuric acid and G. Frederick Smith analytical reagent ceric acid sulfate. Water from a Barnstead still was purified and stored in silica vessels. All irradiations were made in a 900 curie cobalt-60 γ-ray source. The dose rate was determined by the Fricke dosimeter assuming that 15.60 ferrous ions were oxidized per 100 e.v. of absorbed energy.[5] The additional energy absorption due to the added solute was calculated.[6] The yield, G(product), defined as the number of ions formed per 100 e.v. of absorbed energy, was calculated from the total absorbed energy. Analytical measurements of ferric ion concentrations were made directly on a Cary Recording Spectrophotometer at 3050 Å. using a molar extinction coefficient of 2240 at 25.°[5] Determination of the S.T.P. volume of the molecular hydrogen formed was made by ignition with oxygen on a platinum filament. The volume of solutions irradiated was determined by weight after the irradiation and hydrogen analysis.

The hydrogen yields were determined at two doses, 0.6×10^{20} e.v. and 1.2×10^{20} e.v. in solutions 0.001, 0.003, 0.008, 0.026, 0.064 and 0.10 molar Ce^{IV} and two acidities 0.4 and 0.8 M H_2SO_4. The data in Table I illustrate the suppressive effect of ceric ion concentration on the hydrogen yield and may be expressed by the least squares determined equation $G(H_2) = -0.21 [Ce^{IV}]^{1/3} + 0.44$. The concordance of the data indicates that the hydrogen yields in 0.4 and 0.8 M H_2SO_4 solutions containing Ce^{IV} ions are the same. The hydrogen yields reported for oxygenated 0.4 M H_2SO_4 solutions containing 0.01 and 4×10^{-4} M ceric ion[7] are in agreement with these experimentally determined values when corrections are made for the suppressive effect of oxygen. Recalling the mechanism of ceric reduction in 0.4 M H_2SO_4 solution[8] and that ions reducible by H atoms lower the hydrogen yield one may see readily that a decrease in the hydrogen yield will cause an equivalent increase in the cerous yield. Appropriate calculations for 400 and 1000 micromolar ceric solutions 0.4 M H_2SO_4 show that the $G(Ce^{III})$ should be 2.37 and 2.38, respectively. These calculated values for the Ce^{III} formation in 400 and 1000 micromolar ceric solutions are in agreement with the values $G(Ce^{III}) = 2.39$ (Sworski)[9] and $G(Ce^{III}) = 2.37$ (Masters and Challenger).[10] Since the extrapolated hydrogen yield at zero solute concentration is 0.44 ± 0.01 one may conclude that the $G(H_2)$ is the same and equal in 5×10^{-6} to 0.8 M H_2SO_4 solu-

TABLE I

HYDROGEN YIELDS OBSERVED IN Ce^{IV}–H_2SO_4 SOLUTION

Initial Ce^{IV}	0.4 M H_2SO_4	0.8 M H_2SO_4
None	0.45[a]	0.44[a]
0.001	.41[b]	.41[b]
.003	.40[b]	.40[b]
.008	.40	.40
.026	.38[b]	.39[b]
.064	.34	.35
.10	.34	.34

[a] Contained 10^{-4} M KBr. [b] Single determinations.

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[1] Work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation.

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tions. The dependence of $G(H_2)$ on a function of the ceric concentration indicates that the presently accepted theoretical yield of cerous ion [$G(Ce^{III})$ = 2.34] may be obtained only in an infinitely dilute ceric solution.

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OAK RIDGE, TENN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY CHEMISTRY DIVISION]

Adsorption of Negatively Charged Complexes by Cation Exchangers[1]

BY KURT A. KRAUS, DONNA C. MICHELSON AND FREDERICK NELSON

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Strong adsorption of some negatively charged complexes by cation-exchange resins is demonstrated. This adsorbability, which is negligible at low ionic strength, increases rapidly with ionic strength, is much greater from salt than from acid solutions and is strongly dependent on the type of the metal complex. With concentrated chloride salt solutions, distribution coefficients larger than 10^6 were found for trace amounts of the anionic complexes (MCl_4^-) of Fe(III), Ga(III) and Au(III). Under these conditions adsorbability of the anionic complexes of Sb(V) and Tl(III) is considerably less and that of the complexes of Mn(II), Co(II), Zn(II), Bi(III) and Sn(IV) is essentially negligible. Use of the adsorption of anionic complexes for separations by cation exchangers is illustrated with several examples.

One usually assumes in the ion-exchange field that cation exchangers adsorb only positively charged ions and anion exchangers only negatively charged ions. These restrictions are tempered by the recognition that, particularly at high ionic strength, substantial electrolyte invasion of the resin may occur and that uncharged species (*e.g.*, organic molecules, bromine, iodine) may be adsorbed; strong adsorption of anions by cation exchangers (or cations by anion exchangers) seems not to have been seriously considered.

Since adsorbability of some negatively charged complexes by anion exchangers is extremely high,[2] the question arose whether part of this high selectivity of the anion exchangers results from interactions of the complexes with the organic network. One might then expect that at least those negatively charged complexes which are very strongly adsorbed by anion exchangers could also be adsorbed by cation-exchange resins. This prediction was verified in a series of adsorption studies with the strongly acidic exchanger Dowex-50. This resin was chosen since it has the same organic network (polystyrene–divinylbenzene) as the Dowex-1 resin used for the earlier anion-exchange studies.

Characteristic features of anion-exchange adsorption of many metal complexes are a rapid rise of adsorbability with increasing salt concentration and a rapid divergence of adsorbabilities between those found in acids and their corresponding salts.[2,3] In the search for adsorption of anions by cation exchangers, media of very high ionic strength were therefore selected and data in acid and salt media compared.

Experimental

Adsorbabilities were determined at room temperature (25 ± 1°) by batch equilibration and column methods. In the equilibration method aliquots of the solutions were shaken for several days with weighed amounts of resin. From analyses of the solution phase before and after equilibration, distribution coefficients D (amount per kg. resin/amount per liter of solution) were computed.

In the determination of large distribution coefficients ($D > 500$), a modified column technique (pre-loaded column method) was used.[4] In this method the material is first adsorbed uniformly on a weighed amount of resin, preferably under conditions where the distribution coefficients are only moderately high. The pre-loaded resin is then transferred to a column, and the solution of interest is passed through the bed. Equilibrium between solution and resin bed normally is rapidly attained, and distribution coefficients may be computed from the known initial concentration of the material in the resin and from analyses of the effluent solutions. One may assume that equilibrium has been reached, when, after a change in eluent, the concentration of the material is the same in successive samples, provided, of course, one operates under conditions where the effluent composition is independent of flow rate. This technique is particularly convenient for comparative measurements at constant loading. When the distribution coefficients are high, a large number of column volumes of solution may be passed through the bed before the composition at its exit end, where final equilibration occurs, has changed significantly.

All analyses were carried out radiometrically. Liquid samples, in small test-tubes, were counted in a well-type scintillation counter (sodium iodide crystal, thallium activated). The following tracers were used: Mn^{54} ($T_{1/2}$ = 300 d.), Co^{60} ($T_{1/2}$ = 5.24 y.), Zn^{65} ($T_{1/2}$ = 245 d.), Ga^{67} 77.9 h.), Sn^{113}–In^{113} ($T_{1/2}$ = 119 d. and 1.74 h.), Sb^{124} ($T_{1/2}$ = 60 d.), Au^{198} ($T_{1/2}$ = 2.7 d.), Tl^{204} ($T_{1/2}$ = 3.5 y.), and Bi^{210} ($T_{1/2}$ = 5 d.).

The tracers, except Ga^{67}, were obtained from and analyzed for purity by the Radioisotopes Division of ORNL. $Gallium^{67}$ was prepared by proton bombardment of zinc and separated from the target material by ether extraction. The purity of the tracer was checked by following its half-life.

A strongly acidic cation exchanger of the polystyrene–

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(1) This paper is based on work done for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. It is based on work summarized in the Chemistry Division Semiannual Progress Report, ORNL 2046, July to December 1955.

(2) See *e.g.*, K. A. Kraus and F. Nelson, "Anion Exchange Studies of the Fission Products," Vol. VII, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, United Nations, New York, N. Y., 1956, pp. 113, 131.

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(4) See also ref. 3c, p. 35.