

*cis* compound in dilute hydrochloric acid. This is shown by the fact that the infrared spectra of the corresponding pairs are identical, and in turn these spectra are identical with those of the original preparations described in the Experimental section. The neutralization of the 0.1 *N* hydrochloric acid solution of the *trans* inner complex yields an inner complex whose infrared spectrum is identical with that of the *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate. The *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is easily isomerized to the *trans* compound simply by heating for 15 minutes at 140°. The *trans* compound thus obtained has the same infrared spectrum as the one from the original preparation. When the *cis*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is dissolved in 1 *N* hydrochloric

acid, heated on the steam-bath for 15 minutes, and neutralized with sodium hydroxide, the *trans*-bis-(pyridine-2-aldoxime) platinum(II) dihydrate is isolated as is evidenced again by its characteristic infrared spectrum.

From these results it seems that intramolecular hydrogen bonding and the resultant extra chelate ring formation tend to stabilize the *cis* configuration and serve to isomerize the *trans* inner complex to the *cis* inner complex through the formation of the intermediate monohydrogen compound. The fact that the *cis* compound is converted to the *trans* in more concentrated acid seems to indicate that both oximate oxygens may be protonated and that the resulting dihydrogen species loses the stabilizing influence of the extra chelate formation and thus rearranges to the *trans* configuration.

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## Polymerization in Cobaltic Periodate Solutions<sup>1a</sup>

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Acidified solutions of  $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$  show the presence of two types of periodate ions as evidenced by the fact that a portion, but not all, of the periodate may be removed by precipitation or reduction without changing the absorption spectra. Polymerization of the cobalt species to form a soluble polynuclear complex having a cobalt(III) to periodate ratio of 4:3 occurs at a measurable rate which increases with increasing hydrogen ion concentration. From a 2 *M* perchloric acid solution, a dark green crystalline solid is obtained which has 3 strongly ionized hydrogen ions and 3 iodine atoms per four cobalts. The crystals are soluble in water and have an elemental analysis and equivalent weight leading to a postulated formula  $\text{H}_2[\text{Co}_4\text{I}_3\text{O}_{36}\text{H}_2]$  for their composition.

Recently, Lister and Yoshino<sup>2</sup> have described the preparation and properties of some most interesting compounds, which apparently contain periodate ions coordinated to cobalt (III). Such complex ions should be of general interest because complexes containing strong oxidizing agents as ligands are quite rare, and due to the possible octahedral configuration of the periodate ion, these complexes might show structural resemblance to polynuclear species. For these reasons and because the compounds have not been fully characterized, further investigation seems appropriate.

The sodium salt has been formulated previously as  $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$  or alternatively as  $\text{Na}_6[\text{Co}(\text{H}_2\text{IO}_6)_2(\text{OH})_2] \cdot 8\text{H}_2\text{O}$ . By passing solutions of this salt through hydrogen-form cation exchange resins, Lister and Yoshino have prepared solutions of the corresponding free acid. However, they have shown by spectral studies that in acid solutions the compound undergoes changes at measurable rates. A primary goal of the present work is to elucidate the nature of these changes in order to gain a more detailed knowledge of the structure and properties of the compound.

### Experimental

The sodium salt,  $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2 \cdot 10\text{H}_2\text{O}$ , readily was prepared by using a variation of the Lister and Yoshino pro-

cedure as described: 0.01 mole of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was mixed with 0.02 mole of  $\text{NaIO}_4$  in 900 ml. of water; 0.2 mole of  $\text{NaOH}$  was dissolved in 100 ml. of water and added to the mixture. Immediately, 0.02 mole of  $\text{NaOCl}$  was added with stirring. An emerald green color appeared in the solution and an olive green solid formed. The solution was separated by centrifugation, and the olive colored solid discarded. On treatment of the solution with one-half of its own volume of ethanol, added in small amounts and with constant stirring, the  $\text{Na}_5\text{H}_2\text{Co}(\text{IO}_6)_2$  precipitated. This precipitate (which was oily if the alcohol was added too rapidly) was dissolved in 200 ml. of water and then 200 ml. of 4 *M*  $\text{NaOH}$  was added. After standing 12 to 24 hr., the green crystalline material was collected on a coarse fritted glass filter funnel, washed two times with small portions of cold water, two times with 50% alcohol water mixture and two times with absolute alcohol. The sample was dried by sucking air through, transferred to a desiccator and stored over anhydrous calcium chloride. It was found that 50 ml. of ethanol can be used as a precipitant in place of the  $\text{NaOH}$ .

While a complete analysis of the solid was not obtained, the iodine/cobalt ratio was determined to be 2.0. Furthermore, the spectrum of aqueous solutions of the solid prepared by this procedure is identical with that reported by Lister and Yoshino.

**Cobalt Determination.**—Cobalt was determined spectrophotometrically using an aliquot portion of a solution of known weight of sample. In a typical analysis, one ml. of cobalt solution was pipetted into a 10 ml. volumetric flask, 0.2 ml. of 1 *M*  $\text{H}_2\text{SO}_4$ , 0.2 ml. of 1 *M*  $\text{Na}_2\text{SO}_3$  and 8 ml. of conc. (12 *M*)  $\text{HCl}$  were added. The absorption spectrum then was determined and the optical density at 6900 Å., the long wave length maxima in the  $\text{Co}(\text{II})$  spectra were used to determine the concentration of the unknown by comparison with a calibration curve prepared from known samples.

**Iodine Determination.**—Iodide analysis was carried out using a method outlined by Willard and Furman.<sup>3</sup> Thirty-

(1) (a) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States government. (b) Department of Chemistry, Washington State University Pullman, Wash.

(2) M. W. Lister and Y. Yoshino, *Canadian J. Chem.*, **38**, 45 (1960).

(3) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, pp. 320-321.

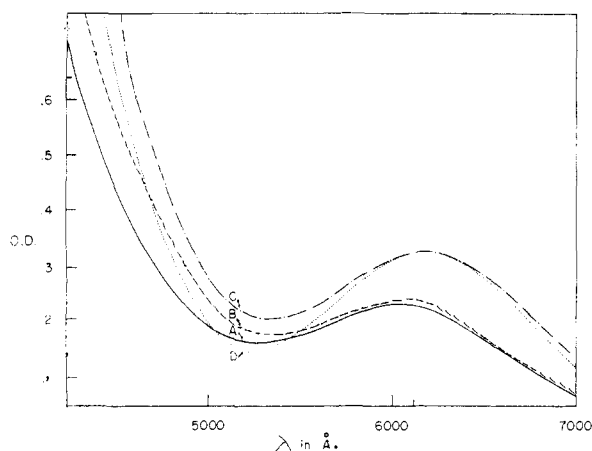


Fig. 1.—Spectra of  $2.8 \times 10^{-3} M$   $[\text{Co}(\text{H}_2\text{IO}_6)_2(\text{OH})_2]^{-5}$  in buffered solutions obtained at  $25 \pm 1^\circ$  with a Cary Model 14 Recording Spectrophotometer employing 1 cm. quartz cells, automatic slit control setting 25, and recorder sensitivity 2. Optical density (O.D. =  $\log I_0/I$ ) is plotted vs. wave length in  $\text{\AA}$ .; curve A,  $\text{pH} = 0.6$ ; B,  $\text{pH} = 4.0$ ; C,  $\text{pH} = 7$ ; D,  $\text{pH} = 9$  or 11. The appropriate buffer solution was used as the blank reference solution in each case.

five to 50 ml. portions of cobalt solutions were added to 50 ml. of water, followed by 25 ml. of  $0.2 M \text{Na}_2\text{SO}_4$  and 25 ml. of  $1.0 N \text{H}_2\text{SO}_4$ . The sample was then boiled gently for 5 minutes to expel the excess  $\text{SO}_2$ . After cooling, 10 ml. of  $0.1 M \text{AgNO}_3$  was added and with stirring the solution was heated to coagulate the precipitate. The silver iodide was washed with  $0.01 M \text{HNO}_3$  by decantation and collected on a porous porcelain crucible, dried at  $125^\circ$  and weighed as  $\text{AgI}$ .

### Results

Solutions of the sodium salt of the periodato-cobalt(III) were reduced, at room temperature, with ferrous sulfate. It was found, as had been reported previously,<sup>2</sup> that five moles of  $\text{Fe}^{++}$  were required per mole of  $\text{Co}(\text{III})$  corresponding to the reduction of  $\text{Co}(\text{III})$  to  $\text{Co}(\text{II})$  and of periodate to iodate. Similarly, reduction at room temperature with sodium iodide required seventeen equivalents of sodium thiosulfate to titrate the liberated iodine per mole of  $\text{Co}(\text{III})$ , corresponding to reduction of  $\text{Co}(\text{III})$  to  $\text{Co}(\text{II})$  and of periodate to iodine. These experiments served to confirm the stoichiometry of the entire solute without, however, specifying the nature of individual species. Furthermore, the results showed that in fact the Co was present in oxidation state +3.

The preparation of the "free acid" as described by Lister and Yoshino by passing a solution of the sodium salt of the bisperiodate complex through a hydrogen exchange resin (Dowex 50) was carried out and, as reported previously, the spectra of this solution were found to change with time. These changes were, however, very slight. Furthermore, the spectrum was found to be a definite function of the  $\text{pH}$  of the solutions. In Fig. 1 and 2 are presented spectra of solutions at various values of  $\text{pH}$ . These spectra were obtained after allowing the solutions to stand for approximately 1 hr. to allow the changes noted by Lister and Yoshino to approach completion.

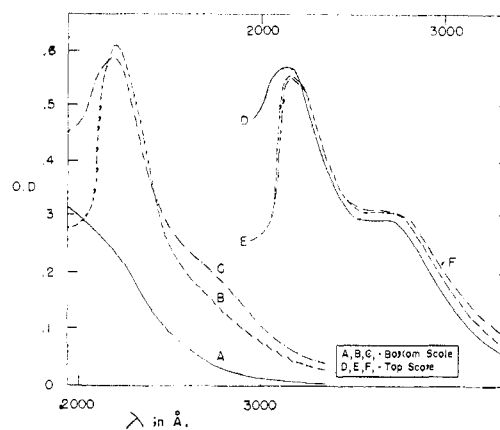
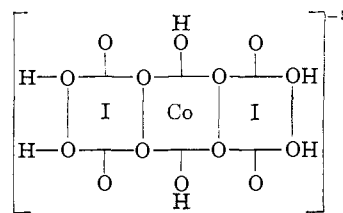


Fig. 2.—Spectra of  $1.8 \times 10^{-5} M$   $[\text{Co}(\text{H}_2\text{IO}_6)_2(\text{OH})_2]^{-5}$  in buffered solutions obtained at  $25 \pm 1^\circ$  with a Cary Model 14 Recording Spectrophotometer employing 1 cm. quartz cells, automatic slit control setting 25, and recorder sensitivity 2. Optical density (O.D. =  $\log I_0/I$ ) is plotted vs. wave length in  $\text{\AA}$ .; curve A,  $\text{pH} = 0.6$ ; B,  $\text{pH} = 4$ ; C,  $\text{pH} = 7$ ; D,  $\text{pH} = 9$ ; E,  $\text{pH} = 11$ ; F,  $\text{pH} = 13$ . The appropriate buffer solution was used as the blank reference solution in each case.

The spectra in the visible region are shown in Fig. 1 where solutions containing total cobalt of  $2.8 \times 10^{-3} M$  were employed. In Fig. 2 are shown the spectra of the far ultraviolet region where the total cobalt concentration was  $1.8 \times 10^{-5} M$ .

The spectra in Fig. 2 are particularly interesting in that they show the appearance of the  $\text{IO}_4^-$  spectra in changing the  $\text{pH}$  from 0.6 to 4, as evidenced by the marked increase in absorption at  $2200 \text{\AA}$ .<sup>4,5</sup> At  $2400 \text{\AA}$ . Crouthamel, *et al.*, noted the appearance of an absorption due to the  $\text{H}_2\text{IO}_6^{-2}$  species. The increased absorption of the cobalt complexes at  $2700 \text{\AA}$ . above  $\text{pH} 7$  probably is due to the appearance of a species similar to  $\text{H}_2\text{IO}_6^{-2}$ . Since this would represent a shift in the absorption band, an explanation would be appropriate. Such a shift in the electron transfer band could be caused by the replacement of one of the hydrogens bound to an oxygen of a periodate by a cobalt(III) ion thus giving rise to an  $\text{H}_2\text{IO}_6^{-3}$  group joined by oxygen bridges to a cobalt(III) rather than to a hydrogen ion. The structure previously has been proposed by Lister and Yoshino and is in agreement with these arguments.



Consideration of spectra attributable to the  $\text{IO}_4^-$  species showed that the similarities between the spectra of the acid solutions of the complex and

(4) C. E. Crouthamel, A. M. Hayes and D. S. Martin, *J. Am. Chem. Soc.*, **73**, 82 (1951).

(5) C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, *ibid.*, **71**, 3031 (1949).

that of periodate were so great as to suggest that some, if not all, of the periodate was not bound to cobalt in the acidic solutions. It was subsequently found that some of the periodate could be removed without affecting the absorption spectrum of the complex solutions in the visible region, where free periodate does not absorb. From acidified solutions of the salt and also from the "free acid" prepared by hydrogen ion-exchange, periodate was removed by two distinct methods: the precipitation of tetraphenylarsonium periodate,  $(C_6H_5)_4AsIO_4$ , and the reduction of periodate by iodide at  $0^\circ$  and titration of the liberated iodine with thiosulfate. Both methods were stoichiometric and agreed quantitatively in measuring the amount of labile periodate. Thus it was found that a definite fraction of the total periodate could be removed without changing the complex species. It was concluded that acidified solutions of the compound contained two kinds of periodate which will be called "labile" and "masked."

It should be noted that the iodide reduction was done at  $0^\circ$  where only the "labile" periodate, but none of the "masked" periodate or the cobalt(III), was reduced to give a sharp end-point. At room temperature, or at  $0^\circ$  in the presence of iron(II) which acts as a catalyst, all the periodate and the cobalt(III) are reduced. A differential titration procedure was therefore possible at  $0^\circ$ . A 10 ml. sample of the acidified solution containing about  $7 \times 10^{-3} M$  cobalt complex was pipetted into a flask cooled in an ice-water bath; 10 ml. of  $0.5 M H_2SO_4$ , 2 g. of solid KI were added, and the sample titrated with  $0.035 N Na_2S_2O_3$  solution to the labile periodate end-point using starch as an indicator, while still keeping the flask in the ice bath. One ml. of  $0.01 M FeSO_4$  was added and the titration continued to determine the total equivalents of oxidizing agent in the sample. By knowledge of the total cobalt and total periodate in the system, the ratio of masked periodate to cobalt(III) was calculated.

The labile periodate in the acidic solutions was quantitatively determined by the above differential titration procedure, and thus it was found that the masked periodate/cobalt ratio increased with time. Employing a solution containing  $5.0 \times 10^{-3} M$  cobalt complex and  $0.1 N H_2SO_4$ , the rate of increase in masked periodate/cobalt(III) was followed by pipetting out samples, quenching them in an ice bath and titrating by the differential titration procedure. Two minutes after mixing, the ratio (masked periodate/cobalt(III)) was 0.07; at 1 hr., 0.38; at 10 hr., 0.53; and at 100 hr., 0.71. The ratio increases at a rate comparable to the spectral changes, and the rate accelerated markedly as acid was increased from  $0.1 M$  to  $1.0 M$ . After a ratio of bound periodate/cobalt(III) of 0.71 was reached, further changes, if any, were too slow to detect. Moreover, essentially the same ratio, 0.70 for masked periodate/cobalt(III), was obtained from the solutions of "free acid" as prepared by the ion-exchange procedure and which were allowed to stand for several days prior to titration. Similarly, the precipitation of the labile periodate as  $(C_6H_5)_4AsIO_4$  showed the resulting solution to

have the same ratio of masked periodate to cobalt(III).

Solutions of the free acid from which all the free periodate had been removed by precipitation as  $(C_6H_5)_4AsIO_4$  were titrated with base using a pH meter. The pH curves obtained were very similar to those of strong acids and thus the final species must be at least a moderately strong acid, with acid dissociation constants exceeding  $10^{-2}$ . Such solutions were subjected to anion exchange, and it was found that the cobalt species behaved as anions even at pH 1.

If saturated solutions of the periodate complex were made approximately  $2 M$  with  $HClO_4$  and allowed to stand, after several days a dark green crystalline solid precipitated. The solution remaining now contained a lower ratio of masked periodate per cobalt(III) than 0.70. Solutions prepared by redissolving the green solid in water contained no labile periodate and had a ratio of masked periodate to cobalt(III) of 0.76. The visible absorption spectra of these solutions differed only slightly from those of solutions before the solid had precipitated.

To obtain a pure sample of this material for further study, samples of the material which precipitated from the acidified periodatocobaltate solutions were redissolved in a minimum amount of water and reprecipitated by making the solution  $2 M$  in perchloric acid and allowing the solution to stand for 24 to 48 hr. After two such precipitations, the crystalline solid was collected on a fritted glass funnel, washed with  $H_2O$ , dried and analyzed quantitatively for cobalt and iodine by the procedures described in the Experimental section. The ratio of iodine to cobalt based on this analysis was 0.76. The empirical formula weight per cobalt atom was 280 and that per iodine atom was 365.

Since the acid species had been shown by ion-exchange to be anionic, it now remained to determine the charge on the complex. By titrating a solution prepared from the crystalline free acid which was of known total cobalt and periodate concentration, it was determined that 0.76 equivalent of hydrogen per cobalt was titrated readily with NaOH. This titration curve was identical with that of an acidified solution of the periodatocobaltate which had been allowed to stand and from which the excess free periodate ion had been removed. Furthermore, on passing a sample of solution prepared from the crystalline free acid through the hydrogen form of a cation exchange resin prior to titrating, it was found that the same volume of NaOH was required to titrate the acidic hydrogens. Thus it was concluded that no ionizable cations other than hydrogen were present in the green solid and that the charge on the anion was  $-0.75$  per cobalt. Thus the acid equivalent weight was 365.

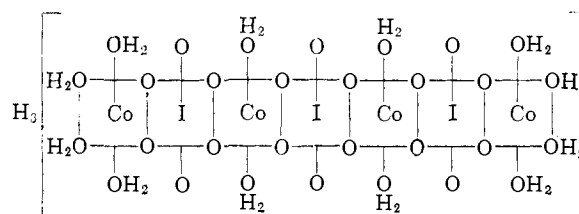
### Conclusions

Because  $Co^{+3}(aq.)$  does not exist for extended periods in solution at room temperature, it must be assumed that in acid solutions of periodatocobaltate, all of the cobalt(III) is somehow bound into complex species. The ratio of masked periodate/cobalt(III) being less than unity and the

fact that the labile periodate can be removed from aged acid solutions without affecting either the absorption spectrum or the stability (with respect to reduction by the solvent) shows that the labile periodate is not responsible for stabilization of the cobaltic state. The explanation indicated is that a polynuclear species is formed which contains more cobalt than iodine atoms. Apparently this polymer is slowly built up from simpler species until an appreciable concentration of the species exists which has an empirical formula containing 4 cobalt atoms and 3 periodate groups with a charge of  $-3$ . This species in turn has limited solubility in  $2 M$  perchloric acid and so precipitates. The species has an average simple formula weight of  $1102 \pm 20$  as determined from all determinations of the cobalt, iodine and free hydrogen ion.

A plausible species which satisfies the requirements of stoichiometry and which has a formula

weight of 1124 is  $H_3[Co_4I_3O_{30}H_{24}]$ . One of the several isomeric structures is



ADDED IN PROOF.—An alternative formulation which is equally probable on the basis of evidence presented here is  $H_3[Co_4I_3O_{24}H_{12}] \cdot xH_2O$  with a structure similar to that determined by H. T. Evans (*J. Am. Chem. Soc.*, **70**, 1292 (1948)) for  $(NH_4)_6[TeMo_6O_{24}] \cdot 7H_2O$ .

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO]

## An Isotopic Exchange Study of the U(IV)–U(V)–U(VI) Equilibrium in Aqueous Perchlorate Solutions<sup>1</sup>

BY B. J. MASTERS AND LARRY L. SCHWARTZ

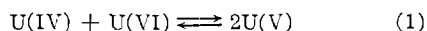
RECEIVED NOVEMBER 17, 1960

Measurements of U(IV)–U\*(VI) exchange have been employed in an investigation of the reaction  $U(IV) + U(VI) \rightleftharpoons 2U(V)$  under conditions of chemical equilibrium in perchlorate media of ionic strength 2.0. A successful separation of this exchange path from the competitive exchange reaction was found possible at U(IV) concentrations below  $0.01 M$  and temperatures of  $25^\circ$  and higher. The equilibrium reaction was found to obey the rate law  $R_{\text{ex}} = k[U^{+4}][UO_2^{+2}][H^+]^{-3}$ , with a rate constant of  $k = 2.13 \times 10^{-7} M^2 \text{ sec}^{-1}$  being observed at  $25^\circ$ . The thermodynamic quantities of activation were found to be  $\Delta H^\ddagger = 37.5 \text{ kcal./mole}$  and  $\Delta S^\ddagger = 36 \text{ e.u.}$  The results are consistent with polarographic measurements of the U(IV)–U(V)–U(VI) equilibrium and of the U(V) disproportionation reaction. The U(IV)–U\*(VI) exchange rate was found to be strongly accelerated by ultraviolet irradiation.

### Introduction

The exchange of uranium isotopes between U(IV) and U(VI) ions in solution has been the subject of a number of cursory investigations,<sup>2</sup> while more comprehensive kinetic studies have been carried out in hydrochloric acid media by Rona.<sup>3</sup> The system also has been studied in sulfuric acid solutions under the influence of external illumination<sup>4</sup> and in mixed aqueous hydrochloric acid–ethanol media.<sup>5</sup>

The formation of uranium(V) in solutions of uranous and uranyl ions, in accordance with the equilibrium



has been demonstrated by Heal<sup>6</sup> and studied

(1) This work was performed under the auspices of the United States Atomic Energy Commission. Presented in part at the 138th A.C.S. Meeting, New York, N. Y., September, 1960.

(2) The following unclassified reports have been issued by the United States Atomic Energy Commission and its contractors: M. B. Allen, RL-4.6.279 (1944); A. Grosse, MDDC-1644 (1948); E. L. King, CB-605 (1946) and MDDC-813 (1947); E. Rona, AECD-1909 (1948); R. W. Woodward, *et al.*, Y-30 (1947) and Y-184 (1948); D. G. Hill, Y-478 (1949).

(3) E. Rona, *J. Am. Chem. Soc.*, **72**, 4339 (1950), and "Radioisotopes in Scientific Research," edited by R. C. Extermann, Vol. II, Pergamon Press, New York, N. Y., 1958, pp. 296–304.

(4) R. J. Betts, *Can. J. Research*, **26**, 702 (1948).

(5) D. M. Mathews, J. D. Hefley and E. S. Amis, *J. Phys. Chem.*, **63**, 1236 (1959), and A. Indelli and E. S. Amis, *J. Am. Chem. Soc.*, **81**, 4180 (1959).

(6) H. C. Heal, *Nature*, **157**, 225 (1946).

quantitatively by Kraus and Nelson.<sup>7</sup> Assuming the uranium(V) ions formed in (1) to be chemically equivalent, this equilibrium should provide one path for exchange between U(IV) and U(VI), and in the absence of other exchange paths, it should be possible to evaluate the rate constant for the forward step in the equilibrium by means of exchange measurements. The separation and measurement of exchange occurring *via* the path represented by (1) has not previously<sup>2–5</sup> been demonstrated and is the subject of the present investigation.

### Experimental

**Materials.**—Distilled water was redistilled from alkaline permanganate solution before use. Sodium bicarbonate, which was used in small quantities for final adjustment of the pH of some of the exchange solutions, was of analytical reagent grade. Analytical reagent grade 70% perchloric acid was filtered through a fine frit and boiled under reduced pressure in a Pyrex distillation apparatus until all yellow-colored impurities (presumably oxides of chlorine) had been removed. Sodium perchlorate was prepared by neutralizing perchloric acid with a slight excess of analytical reagent grade sodium carbonate. The resulting solution was filtered to remove basic precipitates, then acidified slightly and boiled to expel carbon dioxide, after which solid  $NaClO_4$  was obtained by partial crystallization. A stock solution of  $NaClO_4$  was prepared and analyses were performed by evaporating aliquots, drying at  $160^\circ$  and weighing the anhydrous salt. Uranyl perchlorate stock solution was pre-

(7) K. A. Kraus and F. Nelson, *J. Am. Chem. Soc.*, **73**, 2157 (1951)