evaporating the solvent in vacuum, the product was obtained in the form of a pale yellowish viscous oil. This crude butyl phenylbutylphosphinate was refluxed with 200 ml. of concentrated hydrochloric acid for five hours with slow collection of butyl chloride at the distillation head of the hydrolysis apparatus. The residual insoluble oil was separated from the cooled mixture, dissolved in dilute sodium hydroxide and precipitated by means of hydrochloric acid. The resulting phenylbutylphosphinic acid was a viscous oil, which froze to a glass in freezing mixture; the oily character of this product was very similar to that of phenylisobutylphosphinic acid, noted by Arbuzov and Arbuzova,[5] which is an oil in the perfectly dry state and crystallizes only on partial hydration. Phenylbutylphosphinic acid, obtained in 84% yield, had the neutralization equivalent of 202, 203, against the calculated 198, after drying *in vacuo* by repeated evaporations with dry benzene. Conversion to the lead salt gave this substance in the form of colorless, insoluble powder, which contained 34.2% Pb, against calculated 34.4%.

Repetition of the reaction, using methyl iodide instead of butyl bromide, gave after three hours refluxing of the condensation mixture, followed by the above procedure, an 81% yield of methylphenylphosphinic acid, m. p. 133–134°, which agreed with the previous data for this substance.[6]

---

(5) Arbuzov and Arbuzova, *J. Russ. Phys.-Chem. Soc.*, **61**, 1905 (1929).

(6) Pope and Gibson, *J. Chem. Soc.*, **101**, 740 (1912).

THE ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA
RECEIVED MARCH 20, 1950

Adsorption of Protactinium from Hydrochloric Acid Solutions by Anion Exchange Resins[1]

BY KURT A. KRAUS AND GEORGE E. MOORE

The high extractability of protactinium from hydrochloric acid solutions by organic solvents suggested that it can form a neutral chloride complex.[2] The formula of this complex might be $PaCl_5(H_2O)_n$, in *ca.* $3M$ HCl, or a similar neutral complex with probably not more than one or two hydroxide ions per protactinium.[3]

It appeared probable that Pa(V) at a higher chloride concentration could form a negatively charged complex which might be adsorbable by anion exchange resins as were complexes of Ta(V) and Nb(V).[4] This was substantiated in a series of tracer experiments using the quaternary amine resin Dowex-1.

Experimental Procedure and Materials

Adsorption Columns.—Adsorption columns were prepared from 2 mm., i. d. Pyrex tubing, plugged with glass wool to retain the resin. The upper part of the column was in the form of a small reservoir to permit easy addition of solutions and resin. The eluent was placed in a separatory funnel which was joined to the column by means of a small ball joint. The column was filled with resin (200–230 mesh size on wet screening) to a height of 15 centimeters by adding a slurry of resin in water. The resin was washed with water and then with hydrochloric acid of the concentration which was to be used in the experiments. The elutions were carried out with flow-rates of *ca.* 0.2–0.3 ml. cm.$^{-2}$min.$^{-1}$.

Preparation of Pa^{233}.—All experiments were carried out with Pa^{233} tracer (β-emitter, $T_{1/2}$ = 27.4 days)[5] which was prepared by neutron bombardment of thorium metal. After separation from thorium the Pa^{233} was found to be of high purity as shown by its decay curve.

Analysis of Elution Curves.—The β-activity of the eluent was recorded on a Brown "Electronik" strip-chart recorder by passing the solution through a thin-window flow cell which was placed near a G. M. tube. The electronic circuit contained an integrating device and the recorder was of the logarithmic type.[6] In general, the equipment was similar to that developed at the Oak Ridge National Laboratory and described by Ketelle and Boyd.[7]

Batch Experiments.—A series of batch experiments was carried out to determine the distribution coefficients of protactinium with respect to the resin as a function of hydrochloric acid concentration. For this purpose *ca.* 0.1 ml. samples of hydrochloric acid solutions containing Pa^{233} tracer were agitated with 5–20 mg. of resin for one to three days in closed tubes. Agitation was achieved either with a magnetic stirrer using a small length of 10 mil iron wire in a thin glass tube or by mounting the tubes on a vibrator.

The distribution coefficients were determined by direct beta assays of known aliquots of the solution combined with beta assays of weighed, oven-dried portions of the resin. After centrifugation the resin was placed on filter paper to remove excess solution, washed on filter paper with a 50 λ portion of hydrochloric acid of the concentration in question, blotted dry, transferred to a weighed platinum plate and weighed after drying in an oven at 110°. For the β-assays the resin was decomposed with nitric acid followed by ignition.

Results and Discussion

Distribution Coefficients.—It was found from the batch experiment that Pa^{233} is only weakly adsorbed by the anion exchange resin at hydrochloric acid concentrations less than *ca.* $4M$ and that above this concentration the adsorbability rises abruptly. The distribution coefficients (K_d) are given in Fig. 1. K_d is defined by the equation

$$K_d = P_r/P_s \qquad (1)$$

where P_r and P_s are the amounts of protactinium (*e.g.*, in counts/min.) per gram of (oven-dried) resin and per ml. of solution, respectively. It can be seen from Fig. 1 that the reproducibility of the determinations was generally poor and that the distribution coefficients had not reached equilibrium values after one day of equilibration, particularly under conditions where K_d is large. Although the values of K_d are thus only semiquantitative, there is little doubt that protactinium under the conditions studied forms a negatively charged chloride complex.

Since the K_d values become extremely high at very high chloride concentrations, it is unlikely that the charge on the complex is more negative than minus one. The probable equilibrium in the hydrochloric acid range studied is thus

---

(1) This document is based on work performed under Contract Number W-7405 Eng. 26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

(2) K. A. Kraus and Q. Van Winkle, Report ORNL-239, February 1949.

(3) K. A. Kraus and A. Garen, ORNL-65 (March–May 1948) and ORNL-176 (June–August 1948).

(4) K. A. Kraus and G. E. Moore, THIS JOURNAL, **71**, 3855 (1949).

(5) Information from "Table of Isotopes," by G. T. Seaborg and I. Perlman, *Rev. Modern Phys.*, **20**, 585 (1948).

(6) The electrical circuit was prepared for us by F. W. Manning of the Instrument Division of Oak Ridge National Laboratory.

(7) B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

$PaX_5 + nH_3O^+ + (n + 1)Cl^- \rightarrow H_nPaCl^-_{n+1}$ where X represents a chloride, hydroxide or one-half oxide ion.

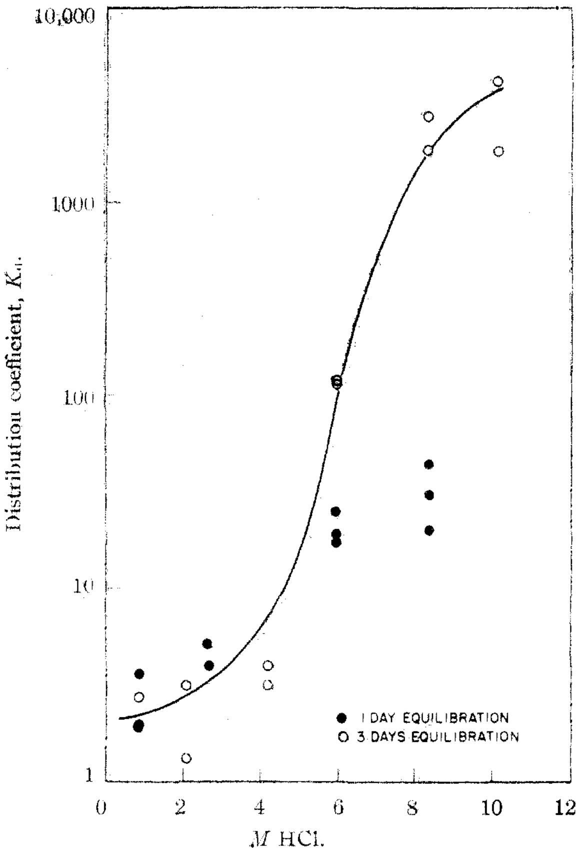


Fig. 1.—Adsorption of Pa(V) on Dowex-1 from chloride solutions.

Column Experiments.—The rapid change of K_d with hydrochloric acid concentration and the low values of K_d at low concentration make it very tempting to use anion exchangers for the purification of protactinium from metal ions particularly under conditions where they have different charges. The usefulness of such methods would depend on the reversibility of the adsorption and complexing processes during the elution time. To establish this reversibility a number of column experiments were carried out and it was found that protactinium at tracer concentrations can be quantitatively adsorbed from 8 *M* hydrochloric acid and washed with large numbers of column volumes of acid of this concentration without moving the band appreciably along the column and furthermore that the protactinium can be eluted with hydrochloric acid of lower concentration. The width of the elution band and the elution time were found to decrease with decreasing hydrochloric acid concentration of the eluent. Reasonably sharp elution bands were found for hydrochloric acid concentrations less than *ca.* 4*M*.

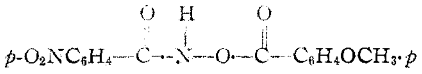
Acknowledgment.—The helpful advice and interest of Dr. George E. Boyd in this work is gratefully acknowledged.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE
RECEIVED MARCH 30, 1950

The Decomposition of Diacylhydroxylamines

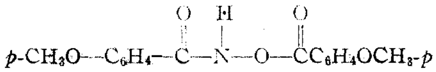
BY JOHN E. LEFFLER

It has been shown recently that *p*-methoxy-*p'*-nitrobenzoyl peroxide decomposes, under favorable conditions, by a polar mechanism involving rearrangement of an assumed oxygen cation intermediate.[1] The favorable conditions required are a medium of high dielectric constant or an acid catalyst. Since the diacyl peroxide rearrangement superficially resembles the Lossen rearrangement, it was of interest to examine the two diacylhydroxylamines (I and II) derived from the peroxide by replacing one oxygen atom by an imino group.



$$p\text{-}O_2NC_6H_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-C_6H_4OCH_3\text{-}p$$

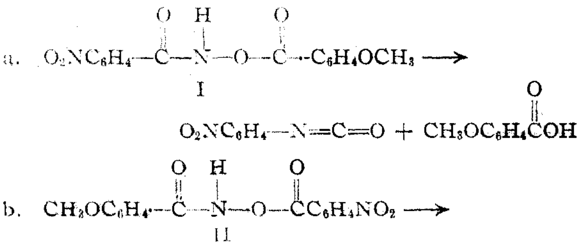
I



$$p\text{-}CH_3O-C_6H_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}C_6H_4OCH_3\text{-}p$$

II

Both of the nitrogen analogs are considerably more stable than the peroxide; they can be recrystallized from hot polar solvents. Heating in nitrobenzene at 150–170° decomposes them but the reaction follows the path of the Lossen rearrangement (reactions a and b) in *both* cases. There is no tendency for I to give anisoyloxy cations (reaction c). When I is refluxed with dioxane and concentrated hydrochloric acid, it is merely hydrolyzed to anisic and *p*-nitrobenzoic acids. Nor is I sensitive to the action of free radicals from anisoyl peroxide; thus a radical chain decomposition (reaction d) starting with the removal of an atom of hydrogen from the imino group may be ruled out. Such a reaction would be analogous to the observed base-catalyzed Lossen rearrangement in which a proton is removed from the imino group.[2]



$$\text{a.}\quad O_2NC_6H_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}-C_6H_4OCH_3 \longrightarrow$$

I

$$O_2NC_6H_4-N{=}C{=}O + CH_3OC_6H_4\overset{O}{\overset{\|}{C}}OH$$

$$\text{b.}\quad CH_3OC_6H_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-O-\overset{O}{\overset{\|}{C}}C_6H_4NO_2 \longrightarrow$$

II

---

(1) Leffler, This Journal, **72**, 67 (1950).

(2) Renfrow and Hauser, *ibid.*, **59**, 2309 (1937).