[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Studies of the Solvent Extraction Behavior of the Transition Elements. II. Isolation of Gram Quantities of Th^{230} (Ionium) from a Pitchblende Residue

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Through utilization of differences in liquid–liquid extractive behavior among the transition elements, approximately sixty grams of Th^{230} (ionium) of isotopic purity averaging 11%, a radionuclide of importance for conversion to Pa^{231} through neutron-irradiation and for tracer applications, has been isolated from an aqueous solution of nitrates resulting from the processing of Belgian Congo pitchblende concentrate for uranium. The Th^{230} (5 g. per ton of liquor) and accompanying scandium, yttrium, rare earths and residual uranium were separated from bulk contaminants and certain radionuclides by use of one solvent system, the residual uranium eliminated by use of a second and the remaining contaminants eliminated by use of a third solvent system. The mass ratio of scandium, the only massive contaminant detectable, to product Th^{230} was less than 0.001. Extraneous alpha activity was less than two tenths of 1% of the total, and beta–gamma contamination was negligible.

Introduction

Two radionuclides of especial interest, found in the waste resulting from the large scale processing of pitchblende for uranium, are protactinium-231 (α-active, 3.4×10^4y[1]) and thorium-230 (α-active, 8.0×10^4y[2]).

Although Pa^{231} has been isolated from natural sources by several workers,[3] the paucity of basic data has made development of processes for its isolation from ore residues difficult. Conversely, lack of adequate supplies of protactinium have made the study of its basic chemistry difficult.

Consequently, gram quantities of Th^{230} (commonly referred to as ionium) would be useful not only in the study of the chemistry of thorium by means of radiochemical techniques but more importantly for transmutation to Pa^{231} through neutron irradiation.[4] This latter use should become a particularly important one, since at secular equilibrium the ionium content of a given sample of uranium ore exceeds the protactinium content by a factor of 58.

In the isolation of Th^{230} from a pitchblende residue, separation of this nuclide from very large relative quantities of elements such as Ca, Mg, Al, Ni and Co, many of which have insoluble fluorides and/or oxalates, as well as from rare earths is involved. Additional difficulties are experienced in removing radioactive contaminants. However, the most difficult removal is that of scandium.

Since the desired nuclide is a trace component of a homogeneous aqueous feed material a liquid–liquid extractive technique was devised.

Experimental

Basic Extraction Studies.—In basic chemistry experiments it was found that Th^{230} at micro-levels, may be extracted into pre-equilibrated tributyl phosphate, $(n\text{-}C_4H_9O)_3PO$, from an equal volume of an aqueous phase which is 0.1 M in HNO_3 and saturated with respect to $Ca(NO_3)_2$ in greater than 99.9% yield. Under the same set of conditions the extraction of micro-level scandium, yttrium and rare earths is greater than 99% complete[5]; however, the extraction of micro-level or macro-level Na, K, Mg, Ca, Sr, Ba, Al, Pb, Co and Ni is negligible, in each case less than 0.1%. It was furthermore found that the Th^{230} could be removed from the tributyl phosphate extract by contacting the extract with aqueous hydrofluoric acid. In general, a precipitate was formed, and always the fraction of the Th^{230} remaining in the organic phase was very small.

An aqueous phase 6 M in NH_4NO_3 and 0.3 M in HNO_3 and an organic phase, prepared by mixing two volumes of dibutoxytetraethylene glycol, $n\text{-}C_4H_9O(C_2H_4O)_4n\text{-}C_4H_9$, with one volume of diethyl ether, pre-equilibrated with respect to this aqueous phase, were found to comprise a suitable system for effecting the separation of Th^{230} from scandium (and at the same time, from yttrium and the rare earths). In such a system, involving equal volumes, the organic phase will contain greater than 90% of the Th^{230}, 15–20% of the scandium and less than 1% of the yttrium or any specific rare earth. A procedure for removal of uranium was based on the fact that from an aqueous solution saturated with respect to aluminum nitrate and buffered with sodium acetate and acetic acid, uranium is preferentially extracted into diethyl ether, Th^{230} remaining nearly quantitatively in the aqueous phase.

Feed Material.—The ionium source was the major aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate for uranium by the Mallinckrodt Chemical Works. This clear liquor, herein referred to as Mallinckrodt waste, is essentially a saturated solution of metallic nitrates having a free nitric acid concentration of approximately 0.4 M and containing approximately 95% of Th^{230} which had been present in the ore concentrate. It contains all of the nitric acid-soluble gross components of the ore concentrate with the exception of the uranium and lead which have been reduced to a small fraction of their original content. The Pa^{231} content varies widely, the average Pa^{231} to Th^{230} mass ratio being approximately 4×10^{-3} as compared with the approximate theoretical value of 17×10^{-3} for the ore concentrate. The Th^{230} content is relatively constant and approximates seven milligrams per liter (or 5 g. per ton).

Isolation of Th^{230}.—A 50-gal. charge of Mallinckrodt waste was mixed intimately for 30 minutes with 2.5 gal. of tributyl phosphate in a conical-bottom, cylindrical, stainless steel contactor of 60-gal. capacity equipped with a twin impeller stirrer. The aqueous (lower) phase was drained to waste, and the tributyl phosphate extract was drained to a conical-bottom, cylindrical, stainless steel contactor of 13.4-gal. capacity in which the composite extract from three runs was mixed for 15 minutes with 7.5 l. of aqueous 1 f hydrofluoric acid. The aqueous (lower) phase containing the dispersed fluoride precipitate was then fed to a solid-bowl continuous centrifuge. The precipitate was stirred with two 100-cc. portions of a saturated aqueous solution of aluminum nitrate, and the resultant slurry was transferred by suction to a polythene container.

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(1) Q. Van Winkle, R. G. Larson and L. I. Katzin, Argonne National Laboratory Report ANL-4095 (January, 1948).

(2) E. K. Hyde, Plutonium Project Report CC-3663 (September, 1946).

(3) A. V. Grosse, *Nature*, **120**, 621 (1927), and G. Graue and H. Kading, *Angew. Chem.*, **47**, 650 (1934), used residues from pitchblende as their source of protactinium. A large number of other workers have isolated small quantities of protactinium from a great variety of uranium ore residues.

(4) The transmutation of Th^{230} to Pa^{231} through neutron irradiation has been demonstrated by E. K. Hyde, Argonne National Laboratory Report ANL-4183 (August, 1943). The Th^{231} formed is a short-lived β-emitter decaying to Pa^{231}.

(5) D. F. Peppard, J. P. Faris, P. R. Gray and G. W. Mason, *J. Phys. Chem.*, **57**, 294 (1953).

The slurries of several runs were combined in a stainless steel beaker and heated at approximately 125° for a period of 4–10 hours with an excess of solid $Al(NO_3)_3 \cdot 9H_2O$. Ten minutes before discontinuance of the heating, anhydrous sodium acetate in the proportion of 100 g. per liter of solution was added. The mixture was allowed to stand at room temperature for 12 hours, and the clear supernate was then transferred by suction to a feed holding tank.

A 1,200-cc. charge of the feed described above was transferred to a two-liter Pyrex contactor, and 36 cc. of glacial acetic acid was added. A mixture of the resultant solution and 500 cc. of a solvent prepared by dissolving 85 cc. of glacial acetic acid in five liters of diethyl ether was agitated for five minutes. After a five-minute settling period the aqueous (lower) phase was transferred by suction to a holding tank. The ether phase was drawn off and set aside to be scavenged for ionium. The aqueous phase was returned to the contactor and stirred with a second 500-cc. portion of the ether solvent, *etc.* In this manner, the aqueous phase was brought in contact with a total of seven 500-cc. portions of ether solvent, each ether extract, exclusive of the first. being transferred to a holding tank for use in the subsequent run. Through this countercurrent method of operation, the need for ionium scavenging was limited to the first ether extract of each run.

Following the seventh ether extraction, the aqueous phase was transferred to a second contactor and mixed with 30 cc. of concd. (approximately 16 *M*) HNO_3. A 400-cc. portion of a solvent prepared by mixing two volumes of dibutoxytetraethylene glycol with one volume of diethyl ether was added, and the mixture was agitated for 15 minutes. Following a settling period of 15 minutes the aqueous (lower) phase was drained to waste. The extract was then brought into contact successively with nine 125-cc. portions of an aqueous scrub initially 6 *M* in NH_4NO_3 and 0.5 *M* in HNO_3, using 10 minutes contact and settling times. This scrubbing was performed in a countercurrent manner, thus restricting the need for ionium scavenging to one scrub per run.

Following the ninth scrub, the extract was transferred to a third contactor where it was brought into contact successively with seven 300-cc. portions of 0.1 *M* HNO_3, using contact and settling times of 10 minutes. In each case the aqueous (lower) phase was transferred to a holding tank from which it was fed to a continuous precipitator to which an excess of concentrated (approximately 15 *M*) aqueous ammonium hydroxide was fed. The resulting composite slurry was transferred continuously to a solid-bowl continuous centrifuge. The precipitate in the centrifuge bowl was then dissolved in a slight excess of approximately 16 *M* HNO_3, and the resulting solution was transferred by suction to a vessel for storage of product.

Discussion

A preliminary volume reduction and gross decontamination from calcium, magnesium, aluminum, nickel, cobalt, *etc.*, results from the tributyl phosphate extraction. (The extraction of Pa^{231} is 30–90% complete.)

A further volume reduction and partial purification is accomplished by agitating the tributyl phosphate extract with aqueous hydrofluoric acid. Under the conditions described the ionium is found nearly quantitatively in the precipitate and the protactinium nearly quantitatively in the aqueous supernate. A considerable decontamination from uranium is achieved at this step.

At the point at which the ionium is prepared for the next solvent extraction step, by dissolving the fluoride precipitate in a saturated aqueous solution of aluminum nitrate, a factor of 800 in volume reduction has been realized. Final decontamination from uranium is obtained by extracting the uranium into diethyl ether after suitably buffering the solution to prevent undue extraction of ionium.

Preliminary removal of contaminant scandium and rare earths results from extracting ionium into dibutoxytetraethylene glycol from the aluminum nitrate phase after overriding the buffer action by the addition of nitric acid. Final removal of these contaminants is accomplished through scrubbing of the dibutoxytetraethylene glycol extract with aqueous NH_4NO_3 solution.

The isotopic purity of the product ionium was found to vary between the limits of 9 and 14%, the major isotope being Th^{232}. After subtraction of the activity due to Th^{227}, 18.9 day α-emitter present as a member of the U^{235} decay series, the purity of the freshly-isolated ionium with respect to α-activity was greater than 99.8%.[6] Within experimental error, there was no extraneous beta–gamma activity.

In terms of one million parts of ionium by mass, no product exceeded the following upper limits: uranium (50), scandium (1,000), yttrium (100), the separate lanthanides (100) and silicon (100). No other elements were detected.[7] On the basis of assays made at various points in the process, it is thought that with the exception of scandium all of the elements listed are present in maximum quantity approximately one hundred-fold lower than the parenthetic values which represent the limits imposed by the assay techniques. Scandium, however, has been found in each of the products.

The yield at the initial extraction step varies from 95 to 99.5%, the variation being due primarily to differences in departure from saturation of the Mallinckrodt waste with respect to metallic nitrates. The yield may be kept at a value consistently greater than 98% by saturating the feed with calcium nitrate.

The ionium yield in the next (fluoride precipitation) step is 94–98% depending upon the ionium to Th^{232} ratio and upon the ionium, rare earths, scandium and yttrium content of the tributyl phosphate extract.

Since the entire quantity of fluoride precipitate is ultimately dissolved in the aluminum nitrate solution, no losses are sustained in this step. The loss of ionium in the number one ether extract, when the system is being operated at the steady state, averages 2.3%, ranging between extremes of 1.5 and 2.7%. By means of simple recycle the loss of ionium in the ether extraction step is reduced to a value well below 0.1%. In the subsequent dibutoxytetraethylene glycol extraction step, in which the diethyl ether serves only as a diluent to lessen the time required for adequate phase disengagement, the loss of ionium to the aqueous phase is less than 0.1%.

The loss of ionium in the number one ammonium nitrate scrub, when the system is being operated at the steady state, averages 2.8%, ranging between extremes of 2.2 and 3.6%. These scrubs

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(6) The authors are indebted to J. F. Mech of this Laboratory for the α-pulse analyses. The instrument is described by A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, "National Nuclear Energy Series," Div. IV, Vol. 14B, Paper 16.8 (1949).

(7) The authors are indebted to J. P. Faris of this Laboratory for the assays performed by the copper spark technique described by M. Fred, N. H. Nachtrieb and F. S. Tomkins, *J. Opt. Soc. Am.*, **37**, 279 (1947). G. R. Price, A.E.C. Declassified Document AECD-2677 (August, 1949), and G. R. Price, R. J. Ferretti and S. Schwartz, A.E.C. Declassified Document AECD-2282 (September, 1948), describe the technique and the instrumentation for determination of uranium by the fluophotometric technique.

were used as a source of scandium, approximately 40 g. having been recovered to date by a modification of the procedure of Fischer and Bock.[8] The ionium was then recycled to the dibutoxytetraethylene glycol step.

The losses of ionium incurred in the re-extraction and precipitation steps are less than 0.02 and 0.04%, respectively. The loss at the dissolution step is zero.

Consequently, the over-all loss in ionium, making use of simple recycle procedures, is limited essentially to the loss incurred in the initial extraction from the Mallinckrodt waste. The resultant yield is, therefore, 95% or more, depending upon the efficiency of the initial extraction.

In practice, the ionium was not recovered from the aqueous wastes resulting from the fluoride precipitation step by simple recycle of these wastes to the next feed. Instead, these aqueous wastes, which were found to have an average Pa^{231} content of 0.3 mg. per liter were set aside for recovery of Pa^{231}.[9] Following recovery of the Pa^{231}, the ionium was recovered by recycle of the aqueous waste to the initial extraction step.

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[8] W. Fischer and R. Bock, *Z. anorg. allgem. Chem.*, **249**, 146 (1942).

[9] R. Elson, G. W. Mason, D. F. Peppard, P. A. Sellers and M. H. Studier, THIS JOURNAL, **73**, 4974 (1951).

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NOTES

The Non-existence of the "Third Isomer" of *p*-Nitrobenzaldesoxybenzoin

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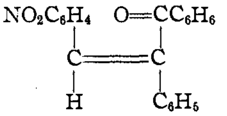
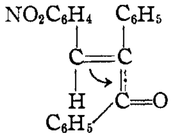
This work stemmed from studies in progress on stereoisomeric (*cis–trans*) pairs of chalcones (benzalacetophenones) substituted in the α- or β-positions, studies dealing with differences in the ultraviolet absorption spectra and their correlation with differences in chemical reactivities of the conjugated systems involved.

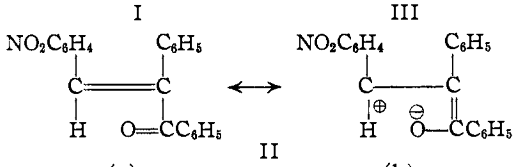
Stobbe[2] in an extensive series of researches has claimed the existence of three isomers in each of two α-phenylchalcone series (*cf.* I, II). He assumes two of these in each series to be *cis–trans* isomers, but he has not explained the nature of the supposed "third isomer" in any instance. Only *cis* and *trans* forms can be accounted for in terms of classical formulations. We thought at first that conjugation and resonance between the styryl system and the carbonyl group in one stereoisomer [presumably the *trans*-chalcone form (II)] might conceivably impart sufficient double bond character to the bond between these two systems so that *cis–trans* isomerism based on planarity of this area of the molecule might prevail, with the carbonyl oxygen pointing inward toward the β-position (II) or outward from it (III).[3] It was later shown[4] that significant resonance between the styryl and carbonyl systems existed only in the *trans*-α-phenylchalcone system,[4] as might have been predicted. Thus the "third isomer" could conceivably be represented (by III) as an example of the kind of isomerism spoken of by Pauling[5] as possible when the double bond character between two conjugated double bonds becomes sufficiently large to maintain planarity of the system. Under the stimulus of this idea (unsound though it was here) careful and extensive attempts were made, unsuccessfully, to reproduce Stobbe's experiments in the *p*-nitrobenzaldesoxybenzoin series. However, the results of these attempts led us to conclude that in this series the "third isomer" does not exist as a compound and that Stobbe's product was in reality a mixture of the normal *cis* and *trans* isomers (I and II).



I



III



II

(a) (b)

Experimental

Each of Stobbe's isomerization reactions on the high-melting isomer where he obtained high yields of the "third isomer," was repeated and the products were fractionally recrystallized with exceeding care (*e.g.*, more than 40 recorded fractionations were made on a single reaction product). In no case was a sample obtained that could not be resolved into one and the other of the same pair of isomers. The best recrystallization solvent was a benzene–isoöctane mixture. Stobbe had used benzene–petroleum ether mixtures, but we found that substitution of isoöctane for petroleum ether diminished creeping of the solvent and advantageously low-

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[1] Holder of Philip Francis du Pont Research Fellowship, 1952–1953.

[2] H. Stobbe and F. Wilson, *Ann.*, **374**, 237 (1910).

[3] *Cf.* a consideration of the conformation of the bromochalcones, R. E. Lutz, D. F. Hinkley and R. H. Jordan, THIS JOURNAL, **73**, 4647 (1951).

[4] W. B. Black and R. E. Lutz, *ibid.*, paper in press.

[5] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 218.