S 76. *Studies of Neutron-deficient Radioactive Isotopes.*

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The technique of investigation of neutron-deficient radioactive isotopes, produced by use of a 60-inch cyclotron, and some preliminary results are recorded.

The investigation of nuclear reactions of high-energy particles from the 184-inch cyclotron, with various elements throughout the Periodic Table, has, during the past few years, been one of the main fields of research of the chemistry group at the Radiation Laboratory, University of California, Berkeley. Quantitative interpretation of results, however, has been made difficult since many new isotopes of indeterminate mass number are produced. Further, many of these radioactive products lie well on the neutron-deficient side of stability, and they decay by orbital-electron capture, often with α-particle branching in the heavier region and positron emission in the lighter elements; the resolution of radioactive species from the complex mixtures, and the determination of distintegration schemes and counting efficiencies necessary in quantitative work, are very difficult. The lack of knowledge of neutron-deficient isotopes was particularly great in the region from praseodymium to gold, and a survey of such isotopes was therefore begun, using the lower-energy particles from the 60-inch Crocker Laboratory cyclotron. Some 40 new radioactive isotopes have now been studied, and several isotopes, previously reported inadequately, have been re-examined. That, in addition to increasing the knowledge of radioactive isotopes, such studies can facilitate research in other fields of science, is shown by the use of the 185-day gold isotope ^{185}Au (Wilkinson, *Physical Rev.*, 1949, **75**, No. 7) as a tracer in studies on arthritis.

Bombardments.—The 60-inch cyclotron is particularly suitable for research on, and production of, radioactive isotopes. The cyclotron produces 10-Mev. protons, 19-Mev. deuterons, and 38-Mev. helium ions, with deflected beams of several microamperes, enabling the formation of radioactive isotopes by reactions such as d, p; $dn, 2n, 3n$; pn; d, α; $d, n, 2n, 3n$; α, pn; $\alpha, p2n$, etc. Using internal or probe targets, beams of 200—300 microamperes of deuterons can be obtained, for example, and large activities of radio-isotopes thereby produced. In the present work, the external, *i.e.*, deflected beam of the cyclotron has been used exclusively, since use of the circulating beam requires special target materials capable of withstanding the heating effects resulting from dissipation of large beam currents. Elements have been bombarded as metal foils, where available, or as oxides. The latter were spread over a grooved copper plate which could be water-cooled. Where small quantities of material, *e.g.*, rare-earth oxides such as lutecium oxide, were available, a small platinum boat of area about 1 sq. cm. was soldered to a small water-cooled copper plate to form an " interceptor " target, which was then placed so as to absorb about one-third of the cyclotron beam. Oxide targets were prepared in the holders, by wetting the powder with sodium silicate solution, and subsequently drying it under

an infra-red lamp. Such bonded targets have withstood over 100 microampere-hours of 19-Mev. deuterons without loss. All oxide targets were covered with 0·2-mil tantalum foil as additional protection.

Where bombardments were desired with particles of energy lower than those produced by the cyclotron, tantalum foils of various thicknesses, calculated from range–energy relations for deuterons, protons, and helium ions in matter, were placed before the target to reduce the beam energy. A 5-mil tantalum foil, for example, reduces the energy of the helium ion beam from 38 to 20 Mev.

Chemical Procedures.—After bombardments had been made, the target material was dissolved in acid, and the radioactive isotopes being investigated were chemically separated by using isotopic carrying on added inactive carriers. Except in the case of the rare-earth elements, where chemical separation was made by means of ion-exchange resin columns, conventional chemical methods of precipitation, solvent extraction, etc., were used. The rare-earth separation procedure is described elsewhere in detail (Wilkinson and Hicks, *ibid.*, No. 9), but in brief is as follows.

A 20 × 0·4 cm. column of Dowex-50, a sulphonated hydrocarbon resin of combining weight about 200, was employed. About 5—10 mg. of rare-earth oxide dissolved in hydrochloric acid pH 0·5—1 were first adsorbed on about 0·2 ml. of resin. This resin was then transferred to the top of the column, through which was then passed a solution of 0·25M-citric acid adjusted to pH 3·05 with aqueous ammonia. The ionic strength of all solutions was held to a minimum in order to achieve best separation. For a drop size of about 0·03 ml., the flow rate of citrate eluant solution was approximately one drop in 4 minutes. Under these conditions the rare earths are eluted from the top resin band and move down the column, lutecium being the first to leave the column, followed by the other rare earths in order of decreasing atomic number. The eluate was collected in small test-tubes held in a perforated wheel which was rotated automatically to bring a tube under the column at predetermined time intervals, *e.g.*, every 15 minutes. The radioactivity of the various tubes was checked during column runs, and the activity plotted against sample number; inactive rare earths were estimated spectroscopically by the arc method. When the quantity of rare earth, measured by either method, is plotted thus, a series of elution peaks is obtained, allowing selection of tubes containing pure rare-earth fractions. Separation factors of over 1000 were obtained between neighbouring elements in many separations.

The general method of approach to the problems can best be shown by an example. About 20 mg. of holmium oxide were bombarded with 38-Mev. α-particles. After an initial chemical purification of the rare-earth fraction by repeated precipitation from hot 3N-nitric acid solution by addition of hydrofluoric acid (the precipitated fluoride was dissolved in concentrated nitric acid saturated with boric acid, and the hydroxide precipitated by ammonia and then redissolved in nitric acid for the next fluoride precipitation), a standard solution was prepared in 1 ml. of dilute hydrochloric acid. Aliquots of this solution were taken (*a*) for direct measurements of radioactivity by aluminium and lead absorption and for decay, (*b*) for estimation of the chemical yield, *i.e.*, for the fraction of bombarded material recovered, and (*c*) for separation on the ion-exchange column.

Where the chemistry of radio-isotopes produced is radically different from that of the target, *i.e.*, in cases other than the rare earths, or in deuteron bombardments of rare earths where radioactive isotopes of adjacent elements are formed simultaneously, chemical separation must in general be performed before radioactive measurements are made. In the holmium bombardment now considered the only activities in the unseparated rare-earth fraction were identical with those obtained in the column-separated thulium and were produced by α,xn reactions; any α,pxn reaction would lead to stable erbium isotopes. Radioactive measurements without previous chemical separation have been made where short-lived activities were produced by proton or α-particle bombardment, or in deuteron bombardments where the products of the d, p and $d,p2n$ reaction with the target nucleus were known.

Radioactive Techniques.—In the present research, neutron-deficient radioactive isotopes have been studied almost exclusively. Decay can thus occur by orbital-electron capture, together with emission of positive electrons, and possibly negative β-particles where the radioactive isotope is "shielded" between two stable isotopes, *e.g.*, 120-day ^{174}Lu. The radiations emitted are therefore almost invariably complex, consisting of L and KX-radiation from orbital-electron capture and conversion of soft γ-rays, γ-radiation of various energies, conversion electrons, and possibly positive and negative β-particles. Although some isotopes have very complex disintegration schemes, with several excited or metastable levels in the

daughter nucleus following orbital-electron capture, *e.g.*, the 64-hour ^{182}Re (Wilkinson and Hicks, *ibid.*, 1948, **74**, 1733), yet others, *e.g.*, the 140-day ^{181}W (Wilkinson, *Nature*, 1947, **160**, 864) have comparatively simple decay schemes and emit X-rays only. Much information on modes of disintegration can, however, be obtained from simple techniques of absorption measurements in aluminium and lead foils. A crude β-ray spectrograph provides information on the sign and nature of electron radiations and in conjunction with absorption measurements allows a reasonable approximate estimate of decay schemes. This instrument consist of a small mica window counter placed on a line with the radioactive source at a distance of 4 cm. In the field from an electromagnet surrounding the source and counter holder, the rough energy distribution and sign of electrons can be obtained by altering the strength and direction of the field, respectively. Data on activity and field strengths are recorded automatically. Information on the nature of electron and soft electromagnetic radiation is obtained by the technique (Wilkinson, *loc. cit.*, 1949) of differential absorption in aluminium and beryllium foils. Since the stopping power of elements for electrons is almost independent of atomic number when the absorber thicknesses are expressed in weight per unit area, whilst that for electromagnetic radiation increases rapidly with increasing atomic number, measurements with aluminium foils give the gross absorption of electrons and soft electromagnetic radiation; if a beryllium foil of thickness sufficient to remove any electrons present is placed over the sample, and the aluminium absorption repeated, the absorption curve for soft electromagnetic radiation is obtained. In the region from neodymium to gold, the mean half-thickness for absorption of L X-radiation varies from ~6 mg./cm.^{2} aluminium and 200 mg./cm.^{2} beryllium to ~30 mg./cm.^{2} aluminium and ~3800 mg./cm.^{2} beryllium. The average energy of K X-radiation in this region ranges from ~38 to ~70 Kev., and K X-rays appear as hard background in aluminium absorption measurements. Where electrons and electromagnetic radiations may have comparable half-thicknesses in beryllium, *e.g.*, for electrons of a few tenths Mev. and tin K X-radiation, the problem of resolution is complicated and requires complete absorption measurements down to γ-ray background using both aluminium and beryllium absorbers; a knowledge of electron energies from a crude β-ray spectrograph, or of expected X-ray energies, is of great assistance in such cases. An alternative method is to use a magnetic field to remove electrons and to measure the electromagnetic radiation directly.

Absorption of hard electromagnetic radiation is obtained by using lead absorbers. In order to reduce spurious effects due to scattering, counters used for these measurements are placed in air, without the usual lead housing. The active sample, mounted in low geometry, is sandwiched between beryllium absorbers to remove electrons, and a further beryllium absorber of thickness sufficient to stop Compton and photo-electrons produced in lead is placed immediately below the counter window. Lead absorbers are then inserted between the beryllium foils. By this approach, energies for X-rays and γ-rays have been obtained from lead-absorption measurements, which agree well with those obtained by more accurate methods. It is to be noted, however, that resolution of radiations of similar energies is impossible by lead absorption and the measurements given mean absorption half-thicknesses and energies. When aluminium, beryllium, and lead absorption measurements have been made at various times, and the decays of the various radiations followed separately, the absorption characteristics of radioactive isotopes, if more than one species is present, can be made by an appropriate resolution of the curves; the contribution of longer-lived activities is subtracted from earlier gross measurements.

In order to try to obtain a rough idea of the disintegration schemes of orbital-electron-capture isotopes, with the object of calculating the yields in nuclear reactions, the ratios of electrons and electromagnetic radiations are calculated from absorption measurements. Corrections are necessary for absorption of the radiations in the counter window, air gap, etc., and for loss of X-rays by the Auger effect. Back-scattering of electrons from the source is minimised by mounting thin samples of active material on very thin mica or on plastic films. The largest errors result from uncertainties in the counting efficiencies of electromagnetic radiations in the counters used. The counting efficiency of 10-cm. long counters filled with 10 cm. of argon and 0·5 cm. of alcohol for 500-Kev. γ-rays is known to be about 0·5%; it has been assumed that this efficiency is constant to about 40 Kev. The increase in counting efficiency for softer radiation was calculated from the known absorption coefficients for the gas, and values of 12% at 7 Kev. and 2% at 10 Kev. were obtained. From 500 Kev., the counting efficiency again increased, and has been taken as 1% per Mev.

Whilst the ratios of the various radiations thus obtained may be in considerable error in view of the uncertainties, some indication of the decay schemes can be obtained. A single

radiation from the radioactive isotope can then be used as a means of calculating relative yields at various bombarding energies, which, of course, as a means of allocating isotopes are of more value than absolute cross-sections. The measured K X-radiation has, in general, been taken as representing disintegration by orbital-electron capture; corrections were made for X-rays arising from conversion. In some cases, where the radiations are mainly X-rays, the yields, calculated on the assumption that one K X-ray quantum represents one disintegration by orbital-electron capture, probably correspond closely to the absolute cross-section for production of the isotope.

In the example given previously, where holmium was bombarded with α-particles, three new radioactive isotopes were characterised. By reducing the energy of the bombarding particles it was possible to allocate unequivocally, from yield considerations, the three isotopes of half-lives 7·7 hours, 9·6 days, and 85 days respectively to masses 166, 167, and 168. The K X-rays in each case were taken as indicative of orbital-electron capture. The accompanying tables shows the yields, at the various energies, in barns.

Activity.	α-Particle energy in Mev. 38	30	19	Reaction.	Allocation.
7·7 Hours	1·1	5×10^{-4}	—	^{165}Ho α, $3n$	^{166}Tm
9·6 Days	7×10^{-3}	0·1	10^{-3}	^{165}Ho α, $2n$	^{167}Tm
85 Days	10^{-4}	3×10^{-3}	0·2	^{165}Ho α, n	^{168}Tm

The allocation of the 85-day activity was confirmed by production of the isotope by fast neutron $n,2n$ reaction on thulium.

The above techniques have been applied to study of neutron-deficient isotopes of many elements between praseodymium and mercury. A preliminary report on several of the new isotopes has been given (Wilkinson, *loc. cit.*, 1948); detailed reports on platinum and gold activities (idem, *loc. cit.*, 1949), thulium (Wilkinson and Hicks, *loc. cit.*), tungsten (Wilkinson, *loc. cit.*, 1947), hafnium (Wilkinson and Hicks, *Physical Rev.*, 1949, **75**, No. 4), and neodymium (*idem, ibid.*, No. 11) have been published, and reports on new isotopes of several other elements are in the course of preparation.

The contribution of such a study on neutron-deficient isotopes to nuclear systematics is as yet uncertain, and the difficulty of ascertaining the exact disintegration energies of orbital-electron-capture isotopes by measurement of these radiation characteristics precludes significant correlations. It is, however, possible to reach a few empirical conclusions. For instance, nuclei of odd Z and even N, where Z and N are the number of protons and neutrons respectively in the nucleus, have longer half-lives than their neighbours; nuclei of even Z and odd N, and odd Z, even N, appear to have a very low abundance of γ-rays in their disintegration, etc. Further, where radioactive isotopes are " shielded " by stable isotopes, decay by both orbital-electron capture and by negative-β-particle emission should be possible, and has been observed in several cases, *e.g.*, 85-day ^{168}Tm, 120-day ^{174}Lu, 35-min. ^{164}Ho, 5·5-day ^{196}Au. In a few cases some evidence for negative-β-particle emission to a " missing " stable isotope has been obtained from aluminium absorption measurements, but has yet to be confirmed by accurate studies on a β-ray spectrometer. Work is now in progress on this matter and an attempt is being made to produce the " missing " isotope ^{190}Pt by bombardment of iridium with 19-Mev. deuterons, where the d, $3n$ reaction leads to ^{190}Pt. Previous work (Wilkinson, *loc. cit.*, 1949) has set a lower limit of about 500 years for the half-life of ^{190}Pt for decay by orbital-electron capture; it is possible, as discussed by Kohman (U.S.A.E.C. Declassified document AECD. 2060), that ^{190}Pt and some other " missing " β-stable isotope, may be α-active with cosmologically short half-lives, and be non-existent now in Nature for that reason.

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