

CarrierFree Radioisotopes from Cyclotron Targets XII. Preparation and Isolation of Be7 from Lithium

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Carrier-Free Radioisotopes from Cyclotron Targets

XII. Preparation and Isolation of Be⁷ from Lithium

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October 11, 1950

THE radionuclide, Be⁷, produced from lithium by the nuclear reaction¹ Li⁷(p,n)Be⁷ using the 10-Mev proton beam of the 60-in. cyclotron at Crocker Laboratory, has been isolated without added isotopic carrier by a separation procedure based on the radio-colloidal² properties of Be⁷. Other radioisotopes produced concurrently by proton bombardment of lithium are short-lived and had decayed prior to the separation reported here. The principal radioactive by-product observed was 112-min. F¹⁸ produced¹ by proton bombardment of the small amount of oxygen which was present as lithium oxide on the target surface.

Five grams of c.p. lithium metal³ was pressed onto a grooved water-cooled copper plate and bombarded in vacuum for 120 μ a hr. at an average beam intensity of 8 μ a. The bombarded lithium was dissolved in 100 ml of water with the gradual addition of dilute HCl. The acid solution was filtered and adjusted to pH 9 with dilute NH₄OH.⁴ This "solution" containing lithium hydroxide, ammonium hydroxide, and Be⁷ presumably as a radiocolloid, was slowly drawn through a Pyrex sintered-glass filter, the pore size of which was of the order of 5 microns. Over 90 percent of the carrier-free Be⁷ remained adsorbed on the glass filter disk.⁵ After washing the filter with 2 ml of water, which removed less than 5 percent of the activity, the Be⁷ was quantitatively removed with 2 ml of 0.1 N HCl. The resultant solution after neutralization was used as a tracer for biological studies. Approximately 30 minutes were required for the separation which had an over-all yield of approximately 90 percent. The Be⁷ was identified by the 52-day half-life and 0.48-Mev gamma-ray previously reported.^{6,7}

We wish to thank Professor G. T. Seaborg for helpful suggestions and Mr. T. Putnam, Mr. G. B. Rossi, and the crew of the Crocker Laboratory Cyclotron for bombardments.

* This document is based on work performed under Contract No. W-7405-eng-48-A for the AEC.

¹ G. T. Seaborg and I. Perlman, Rev. Mod. Phys. **20**, 585 (1948).

² O. Hahn, *Applied Radiochemistry* (Cornell University Press, Ithaca, New York, 1936).

³ Beryllium could not be detected by spectrographic analyses.

⁴ Previous experiments had shown that between pH 2 and pH 9, the amount of Be⁷ which could be removed by filtration increased with pH.

⁵ Filtration through Whatman No. 40 removed only 30–50 percent of the Be⁷.

⁶ E. Segrè and C. E. Wiegand, Phys. Rev. **75**, 39 (1949).

⁷ S. Rubin, Phys. Rev. **69**, 134 (1946).

an ammonium hydroxide—hydrogen peroxide solution containing the target element and the concurrently produced radioisotopes of calcium and vanadium.

The titanium target (c.p. metal³ powder supported on a copper target plate with 0.25-mil platinum foil) was bombarded for 100 μ a hr. at an average beam intensity of 20 μ a. After aging for 24 hours, the bombarded titanium metal powder (approximately 1 g) was dissolved in 40 ml of 18 normal sulfuric acid containing five percent 16 normal nitric acid. A small amount of undissolved inactive material was removed by centrifugation. The supernatant was slowly added to 200 ml of 8 normal ammonium hydroxide containing 15 ml of 30 percent hydrogen peroxide to give a clear yellow "solution" of the following composition: (1) titanium as the soluble pertitanate, (2) radiocalcium, (3) radiovanadium as pervanadate, (4) radioscandium as radiocolloidal aggregates.^{2,4} This "solution" was then passed through two consecutive Whatman No. 42 filter papers which retained over 95 percent of the scandium activity as adsorbed radiocolloid. After washing with 10 ml of water, the scandium activity was quantitatively removed in 10 ml of 1 normal hydrochloric acid which after neutralization with the ammonium hydroxide—hydrogen peroxide solution was again passed through filter paper. Three such cycles gave a hydrochloric acid solution of carrier-free radioscandium containing less than 2 gamma of titanium. In a chemical separation performed on this final fraction using added scandium, calcium, titanium, and vanadium carriers, over 98 percent of the activity was recovered in the scandium fraction.

The decay was followed for 45 days and showed initially a composite 2.5-day half-life corresponding to the shorter-lived¹ scandium isotopes (2.2-day Sc⁴⁴, 3.4-day Sc⁴⁷, 44-hour Sc⁴⁸). Twenty-four hours after bombardment, absorption measurements in aluminum showed the 1.4-Mev beta-particle of 3.9-hour Sc⁴⁴ which is produced⁵ by isomeric transition from 2.2-day Sc⁴⁴. The gamma-radiation had a half-thickness of 11.0 g/cm² in lead. Thirty-six days after bombardment, the activity had an approximately 80-day half-period; aluminum absorption measurements showed the 0.36- and 1.5-Mev beta-particles previously reported⁶ for 85-day Sc⁴⁶.

We are grateful to Professor G. T. Seaborg for helpful suggestions and Mr. T. Putnam, Mr. G. B. Rossi, and the crew of the 60-in. cyclotron for the bombardments.

* This document is based on work performed under Contract No. W-7405-eng-48-A for the AEC.

¹ G. T. Seaborg and I. Perlman, Rev. Mod. Phys. **20**, 585 (1948).

² O. Hahn, *Applied Radiochemistry* (Cornell University Press, Ithaca, New York, 1936).

³ Scandium could not be detected by spectrographic analyses.

⁴ M. H. Kurbatov and J. D. Kurbatov, J. Chem. Phys. **13**, 208 (1945).

⁵ H. Walke, Phys. Rev. **57**, 163 (1940).

⁶ Walke, Williams, and Evans, Proc. Roy. Soc. (London) **A171**, 360 (1939).

Carrier-Free Radioisotopes from Cyclotron Targets

XIII. Preparation and Isolation of Sc 44, 46, 47, 48 from Titanium

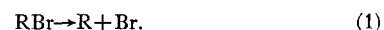
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Experimental Medicine and Radiology; University of California,*
Berkeley and San Francisco
October 13, 1950

THE radioactive¹ scandium was prepared by bombardment of natural titanium with 20-Mev deuterons in the 60-in. cyclotron at Crocker Laboratory. At this energy, radioscandium is produced by the nuclear reactions Ti⁴⁶(d, α)Sc⁴⁴, Ti⁴⁶(d,2p)Sc⁴⁶, Ti⁴⁷(d, α n)Sc⁴⁴, Ti⁴⁷(d,2p)Sc⁴⁷, Ti⁴⁸(d, α)Sc⁴⁶, Ti⁴⁸(d,2p)Sc⁴⁸, Ti⁴⁹ × (d, α n)Sc⁴⁶, Ti⁴⁹(d, α)Sc⁴⁷, Ti⁵⁰(d, α n)Sc⁴⁷, Ti⁵⁰(d, α)Sc⁴⁸; long-lived radiocalcium and radiovanadium are produced concurrently by the reactions: Ti⁴⁸(d, α p)Ca⁴⁶, Ti⁴⁸(d,2n)V⁴⁸, Ti⁴⁸(d,n)V⁴⁹, Ti⁴⁷(d,n)V⁴⁸, Ti⁴⁹(d,2n)V⁴⁹. In the procedure described here, the carrier-free radioscandium is separated as a radiocolloid² from

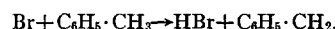
The C—Br Bond Dissociation Energy in Trichlorobromomethane

M. SZWARC AND A. H. SEHON
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October 23, 1950

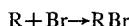
IT was shown in our previous studies^{1,2} that it is possible to estimate the C—Br bond dissociation energy in various organic bromides by pyrolyzing these compounds in a stream of toluene. Under the experimental conditions used in these investigations the bromide molecule RBr dissociates according to Eq. (1)



The bromine atom formed in this process reacts rapidly with the toluene which is used as a carrier gas yielding HBr and a benzyl radical

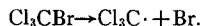


Hence, the rate of formation of HBr measures the rate of the initial dissociation of the molecule RBr. Assuming that the recombination process



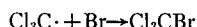
does not require any activation energy, we consider that the C—Br bond dissociation energy is equal to the activation energy of process (1).

We have recently applied this technique for the determination of the C—Br bond dissociation energies in polyhalogenated bromomethanes, and report here the results obtained for trichlorobromomethane. The evidence of present experiments leaves no doubt that the dissociation takes place according to the equation



Hydrogen bromide* was formed in the pyrolysis. Moreover, the formation of dibenzyl is further proof that the dissociation process involves a radical split of the Cl_3CBr molecule. In accordance with the mechanism outlined above the rate of decomposition was measured by the rate of formation of HBr, and we found that the reaction obeys first-order kinetics. The unimolecular rate constant was not affected by the variation of the partial pressure of Cl_3CBr by a factor of 4.5 (from 0.18 to 0.83 mm Hg) and of the time of contact by a factor of 4 (from 0.3 to 1.3 sec.). The rate constant remained also independent of the pressure of toluene when the latter was varied by a factor of 2 (from 10 to 21 mm Hg). The plot of the unimolecular rate constant against $1/T$ is shown in Fig. 1. The straight line corresponds to an activation energy of 48 ± 1 kcal./mole and to a frequency factor of 1.10^{15} sec.⁻¹. The latter value is considered to be an additional proof for the unimolecularity of the dissociation process (1).

Making the usual assumption that the recombination process



does not require any activation energy, we conclude that the C—Br bond dissociation energy in trichlorobromomethane is 48 ± 1 kcal./mole.† Three values for $D(Cl_3C-Br)$ can be deduced from investigations of other workers. The study of the photo-oxidation of trichlorobromomethane by Franke and Schumacher³ leads to a value of about 45 kcal./mole. The studies of bromine exchange reactions makes it possible to estimate the activation

energy of the reaction $Cl_3CBr + Br \rightarrow Cl_3C \cdot + Br_2$; and the results obtained by Miller and Willard⁴ lead to $D(Cl_3C-Br) < 52$ kcal./mole, while those reported by Davidson and Sullivan⁵ to $D(Cl_3C-Br) < 57$ kcal./mole.

The striking point emerging from these studies is the great difference between $D(CH_3-Br)$ and $D(CCl_3-Br)$. For the former bond dissociation energy a value of 68–69 kcal./mole can be deduced on basis of existing thermochemical data and of the known value for $D(CH_3-H)$. Our investigation of the pyrolysis of methyl bromide indicates that $D(CH_3-Br) \approx 67$ kcal./mole. The C—Br bond dissociation energy in trichlorobromomethane is, therefore, lower by about 20 kcal./mole than in methyl bromide. It seems that this decrease is to be attributed mainly to the steric repulsion between the bulky chlorine and bromine atoms in the Cl_3CBr molecule, since our preliminary studies of the pyrolysis of trifluorobromomethane suggests that the difference $D(CH_3-Br) - D(CF_3-Br)$ is about 4 kcal./mole only.

In our opinion two factors contribute to the steric effect responsible for the weakening of the C—Br bond in Cl_3CBr . The strain due to the interaction of the bulky chlorine atoms in any molecule Cl_3CX is released when the molecule dissociates and a planar $Cl_3C \cdot$ radical is formed (see e.g. Brown⁶ and Szwarc⁷). This factor is responsible for the known stability of the Cl_3C radical.⁸ In the particular case of Cl_3CBr the additional decrease in the C—Br bond strength is due to the bulkiness of the bromine atom. The latter effect becomes evident on comparing the difference $D(CH_3-Br) - D(CCl_3-Br) \approx 20$ kcal./mole, with the difference $D(CH_3-H) - D(CCl_3-H)$ † which is equal to about 12 kcal./mole only.

A full account of the determination of C—Br bond dissociation energies in polyhalogenated bromomethanes is in course of preparation.

* It was shown that no HCl was produced within the temperature range used for the thermal decomposition of Cl_3CBr , i.e., 718–827°K.

† If, however, some activation energy were required for the recombination process, the $D(CCl_3-Br)$ would be even smaller than 48 kcal./mole.

‡ $D(CCl_3-H)$ is estimated at about 89 kcal./mole from the data of Schumacher *et al.* See H. J. Schumacher and K. Wolf, *Zeits. f. physik. Chemie B25*, 161 (1934); J. V. Braunwarth and H. J. Schumacher, *Kolloid Zeits.* **89**, 184 (1939).

¹ M. Szwarc and B. N. Ghosh, *J. Chem. Phys.* **17**, 744 (1949).

² Szwarc, Ghosh, and Sehon, *J. Chem. Phys.* (to be published).

³ W. Francke and H. J. Schumacher, *Zeits. f. physik. Chemie B*, **42**, 297 (1939).

⁴ A. A. Miller and J. E. Willard, *J. Chem. Phys.* **17**, 168 (1949).

⁵ N. Davidson and J. H. Sullivan, *J. Chem. Phys.* **17**, 176 (1949).

⁶ H. C. Brown, *et al.*, *J. Am. Chem. Soc.* **67**, 378 (1945) and following papers.

⁷ M. Szwarc, *Disc. Faraday Soc.* **2**, 39 (1947).

⁸ M. S. Kharash *et al.*, *J. Am. Chem. Soc.* **69**, 1100, 1105 (1947).

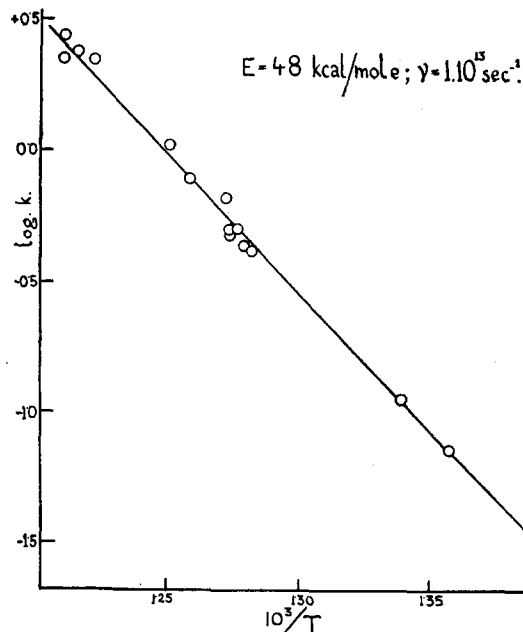


FIG. 1.

Lattice Frequencies of Benzene Crystal

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October 23, 1950

FROM the polarization characteristics of the Raman lines of crystalline benzene Fruhling¹ has recently reported in this journal that the 63 (ν_2) and 105 cm^{-1} (ν_4) lines arise from the rotational oscillations about the two axes of inertia situated in the plane of the molecule (hereafter designated as I) and that the 35 (ν_1) and 69 cm^{-1} (ν_3) lines arise from those about the hexagonal axis (hereafter designated as II).

Although the assignment of these lines is not discussed in detail in his paper, the conclusion does not seem to be reconcilable with the Raman measurements recently made by one of us (I.I.) from -10° down to $-190^\circ C$. In this temperature range all these lines change their frequencies linearly with the absolute temperature T : $\nu_1 = 69 - 0.100T$, $\nu_2 = 89 - 0.083T$, $\nu_3 = 112 - 0.127T$, $\nu_4 = 141 - 0.128T$ cm^{-1} .

The ν_4 -line has almost the same intensity as the ν_2 -line at lower temperatures but the former becomes more diffuse and weaker