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PRODUCTION OF RADIOACTIVE HALOGENS

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This invention relates to the production of radioactive halogens and particularly to the production of radioactive halogens in which there is a high ratio of radioactive halogen atoms to the corresponding ordinary, inactive atoms.

Radioactive isotopes are isotopes which are unstable and capable of radioactivity for a characteristic period. Such isotopes have application as tracers for a wide variety of medical and industrial problems and also have a number of other uses, for example, as specific therapeutics for certain diseases. Among the most useful of the radioactive isotopes are the radioactive halogens.

In preparing radioactive isotopes in general and radioactive halogens in particular, one of the primary objectives has been to produce a material having a high ratio of radioactive halogen atoms to inactive atoms of the same halogen. In other words, in a preparation of radioactive iodine, for example, it is desirable to have as high a ratio as possible of radioactive iodine atoms to ordinary, inactive iodine atoms. The importance of this becomes apparent if one supposes that such a preparation is fed to a human being for the purpose of determining the existence and location of cancers of the thyroid type. Since such cancerous tissues absorb iodine to a much greater extent than the other tissues of the body, it is possible to determine their location by means of a Geiger counter. However, the ability of parts of the human body to absorb iodine at a given time is limited, so that unless a preparation having a rather high ratio of radioactive iodine atoms to inactive iodine is fed, so that there is substantial radioactive emission from the affected parts, measurements cannot practically be made.

Radioactive halogens may be made by bombarding with neutrons an organic halide such as ethyl bromide to which a small amount of bromine has been added, and subsequently extracting the radioactive bromine along with a relatively large proportion of inactive bromine, with water in which the ethyl bromide is substantially insoluble. It has been found that a large proportion of the activated bromine atoms are freed, in this process, from the ethyl bromide. This is probably due to the fact that when the nucleus of a bromine atom in the ethyl bromide molecule is struck by a neutron, the active bromine is detached from the ethyl bromide and with free bromine present the probability is much greater, owing to the relatively higher concentration of the ordinary bromine atoms, that one of the

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ordinary ones will return to the organic combination, leaving an active bromine atom free.

One defect of the method described above is that since the active and inactive forms of bromine cannot be separated by ordinary chemical methods, both forms are extracted by the water and therefore the ratio of radioactive bromine atoms to inactive bromine atoms in the aqueous extract is relatively low.

According to the present invention, this disadvantage is obviated by adding to the organic halide prior to the bombardment, a free halogen which is chemically distinct from the halogen bound in the organic halide. The chemical distinctness between the two halogens may subsequently be utilized to produce a material in which the aforementioned ratio is relatively much higher by treating the extract containing the radioactive halogen to separate the chemically distinct halogen therefrom. It has been found that with this improved process about 80–85% of the halogen atoms which have been activated are liberated from the halide and that preparations having a ratio of active to inactive halogen in the order of 1:500,000 to 1:50,000 may be prepared.

An important object of the invention is to devise a method for preparing a radioactive halogen by bombarding an organic halide with neutrons, in which a large proportion of the activated halogen atoms are liberated from the organic halide and in which the radioactive halogen produced has a relatively high ratio of radioactive halogen atoms to inactive atoms of the same halogen.

Another object of the invention is to produce a composition of matter in which the aforesaid ratio is in the range of 1:500,000 to 1:50,000.

The invention will be described with particular reference to the production of active bromine by bombarding ethyl bromide to which a small amount of iodine has been added.

The reactions which take place during the bombardment are as follows:

$$C_2H_5Br^{79}+n \rightleftarrows (C_2H_5)+Br^{80}$$
$$C_2H_5Br^{81}+n \rightleftarrows (C_2H_5)+Br^{82}$$
$$(C_2H_5)+I \rightleftarrows C_2H_5I$$

In the foregoing equations Br^{79} and Br^{81} are the ordinary isotopes of bromine and Br^{80} and Br^{82} are the radioactive isotopes of bromine.

About 2 liters of ethyl bromide is placed in a soft glass bottle, about 8–12" high, about 4–8" wide and about 1½–2½" thick. About 4 grams of pure solid iodine is added and the bottle is

placed near the window of the cyclotron to receive a stream of neutron particles generated by the cyclotron. After 2 hours bombardment is stopped and 50 cc. of water is added to the contents of the bottle and the layers which form are separated in an ordinary separatory funnel. If desired the 50 cc. of water may be added in two portions of 25 cc. each and the aqueous extracts may be combined. The extraction with water succeeds in separating the ethyl bromide in the non-aqueous layer. The aqueous extract contains about 80–85% of the active bromine with a certain amount of iodine. The aqueous portion is again extracted with three portions of about 7½ cc. each of carbon tetrachloride which takes up the iodine preferentially and the aqueous portion is again separated. At this stage the aqueous portion has an activity of about 10 millicuries of Br^{82} and about 100 millicuries of Br^{80}, both of which are active. The specific activity of the extract in this experiment is about 1000 times greater than if bromine had been added to the ethyl bromide instead of iodine.

Although the invention has been described with particular reference to the bombardment of ethyl bromide to which free iodine has been added, it is understood that this in no way constitutes a limitation on the scope of the invention. For example, instead of employing ethyl bromide, other alkyl bromides might be used such as $CHBr_3$ (bromoform) and CH_2BrCH_2Br (ethylene dibromide). Also iodine may be added to an alkyl chloride such as CCl_4 (carbon tetrachloride). It is also possible to add a halogen which is more reactive than the halogen bound in the organic halide so long as the concentration of the halogen added is kept quite low to prevent any substantial reaction of the added halogen with the organic halide to liberate from the latter the inactive form of the halogen which it is desired to activate. Instead of separating the alkyl halide from the radioactive halogen by a process of solvent extraction, it is possible to do this by other means, such as by distillation or precipitation methods. If solvent extraction is used, any other solvent in place of water may be used if it effects the desired separation. Instead of separating iodine from the aqueous extract by solvent extraction with carbon tetrachloride, it is contemplated that other solvents may be used or that in place of a solvent extraction process, the iodine may be separated by other methods such as for example by precipitation with a reagent capable of selectively precipitating iodine from a bromine solution.

Since many embodiments might be made of the present invention and since many changes might be made in the embodiment described, it is to be understood that the foregoing description is to be interpreted as illustrative only and not in a limiting sense.

I claim:

1. A process for producing a radioactive halogen of high specific activity which comprises mixing an organic halide with a minor amount of a halogen chemically distinct from and more reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said organic halide from said radioactive halogen liberated therefrom and separating said radioactive halogen from said added halogen.

2. A process for producing a radioactive halogen of high specific activity which comprises mixing an alkyl halide with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said alkyl halide from said radioactive halogen liberated therefrom and separating said radioactive halogen from said added halogen.

3. A process for producing a radioactive halogen of high specific activity which comprises mixing an alkyl halide of 1 to 2 carbon atoms with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said alkyl halide from said radioactive halogen liberated therefrom and separating said radioactive halogen from said added halogen.

4. A process for producing radioactive bromine of high specific activity which comprises mixing ethyl bromide with iodine, bombarding said mixture with neutrons, separating said bromide from said radioactive bromine liberated therefrom and separating said radioactive bromine from said iodine.

5. A process for producing a radioactive halogen of high specific activity which comprises mixing an organic halide with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said organic halide from said radioactive halogen liberated therefrom by extracting said radioactive halogen with a solvent in which said halide is insoluble and separating said radioactive halogen from said added halogen.

6. A process for producing a radioactive halogen of high specific activity which comprises mixing a substantially water-insoluble organic halide with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said organic halide from said radioactive halogen liberated therefrom by extracting said radioactive halogen with water and separating said radioactive halogen from said added halogen.

7. A process for producing a radioactive halogen of high specific activity which comprises mixing a substantially water-insoluble alkyl halide with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said alkyl halide from said radioactive halogen liberated therefrom by extracting said radioactive halogen with water and separating said radioactive halogen from said added halogen.

8. A process for producing a radioactive halogen of high specific activity which comprises mixing a substantially water-insoluble alkyl halide of 1 to 2 carbon atoms with a halogen chemically distinct from and less reactive than the halogen bound in said halide, bombarding said mixture with neutrons, separating said alkyl halide from said radioactive halogen liberated therefrom by extracting said radioactive halogen with water and separating said radioactive halogen from said added halogen.

9. A process for producing radioactive bromine of high specific activity which comprises mixing ethyl bromide with iodine, bombarding said mixture with neutrons, separating said bromide from said radioactive bromine liberated therefrom by extracting said radioactive bromine with water and separating said radioactive bromine from said iodine by extracting the latter with carbon tetrachloride.

10. A method for producing radioactive bro-

mine in high yield with a high ratio of radioactive bromine to inactive bromine including mixing ethyl bromide with about 2 grams of iodine per liter of ethyl bromide, bombarding said mixture with neutrons, separating said bromide from said radioactive bromine liberated therefrom by extracting said radioactive bromine with water and separating said radioactive bromine from said iodine by extracting the latter with carbon tetrachloride.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,161,985	Szilard	June 13, 1939
2,206,634	Fermi et al.	July 2, 1940

OTHER REFERENCES

Szilard et al.: Nature, vol. 134, page 462 (1934).

Bank et al.: Nature, vol. 135, page 99 (1935).

Journal Chemical Society (London) pages 390–393 (1936).

Chemical Abstracts 30, 7027 (1936).

Journal Chemical Society (London), pp. 1273–9 (1939).

Journal American Chemical Society, vol. 64, pp. 1342–6 (1942).