

1

3,214,486

METHOD FOR PREPARING RADIOACTIVE HYDROCARBONS

William P. Doyle, Beacon, and Edward T. Child, Fishkill, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware
No Drawing. Filed June 21, 1961, Ser. No. 118,541
7 Claims. (Cl. 260—676)

The present invention relates to radioactive hydrocarbons and, in particular, to an improved method for preparing radioactive hydrocarbons by a reaction with tritiated water in the presence of boron trifluoride.

Radioactive hydrocarbons are compounds that have one or more radioactive carbon or hydrogen elements in their composition. The present process concerns hydrocarbons containing tritium which is a radioactive form of hydrogen. A hydrocarbon compound containing radioactive tritium can be readily identified at another time or place with a suitable radiation-detection device. Because of this property, radioactive hydrocarbons have many useful purposes, such as providing information on the nature and mechanism of chemical reactions, following the course and extent of a chemical process and the like.

Radioactive hydrocarbons have been made by numerous methods including the hydrogenation of unsaturated hydrocarbons using radioactive hydrogen and by exchange reactions using a source of radioactive hydrogen and a catalyst, such as platinum and silica-alumina. While these methods are effective, they are not as efficient or economical as could be desired. Certain of these methods, moreover, are limited in usefulness to the preparation of radioactive hydrocarbons from unsaturated hydrocarbons and are relatively ineffective for providing radioactive materials from saturated hydrocarbons.

An improved method has now been discovered for preparing radioactive hydrocarbons and mixtures thereof. This method is effective for preparing such materials from both saturated and unsaturated hydrocarbons. Indeed, both saturated and unsaturated hydrocarbons can be simultaneously converted to radioactive hydrocarbons. A further feature of this process is that there is substantially complete utilization of the radioactive element or source thereby providing important economies of operation.

In accordance with this invention, a hydrocarbon having from about 3 to 30 or more carbon atoms in admixture with tritiated water is reacted in the presence of boron trifluoride to produce a tritium-containing hydrocarbon. In this reaction, all of the hydrocarbons employed are converted to radioactive hydrocarbons and all of the tritium is removed from the water and transferred to the hydrocarbons.

A broad range of saturated and unsaturated or olefinic hydrocarbons can be employed in this process, there being no criticality in the type or carbon chain length of the hydrocarbon. More particularly, normal and isoparaffins and normal and isoolefins having from about 3 to 30 carbon atoms, and aromatic hydrocarbons having from 6 to 30 carbon atoms can be employed. Specific effective hydrocarbons include propylene, 1-butylene, 2-butylene, isobutylene, 1-pentene, 2-pentene, 1-heptene, 1-decene, 2-decene, propane, butane, isobutane, pentane, isopentane, heptane, xylene, octane, decane, benzene, toluene, naphthalene and the like.

The various hydrocarbons can be employed alone or in admixture with each other. Mixtures of both saturated, olefinic and aromatic hydrocarbons in any proportion can be utilized since there is no criticality in the composition of the reaction mixture.

2

It is essential to employ tritiated water as a reactant and as a source of radioactive hydrogen in this process. It is also important that the tritiated water have a high specific activity or tritium content in order to effect the production of radioactive hydrocarbons. Concentrated tritiated water is commercially available having a specific activity in the order of 1 curie per gram. Because of the radiation hazard inherent in handling this material, it is desirable to dilute the concentrated tritiated water to a specific activity level that is safer to handle, preferably a lower specific activity in the range of 10^{-3} microcurie per gram to 1 curie per gram.

The present reaction is conducted in the presence of boron trifluoride. Broadly, from about 0.01 to about 5% by weight of boron trifluoride based on the weight of the reactants is employed with the preferred amount being about 0.04% by weight. This reaction is conducted at a temperature in the range of -30 to 100° C. with the preferred reaction temperature being about 85° C. While not essential, pressures from about atmospheric up to about 100 p.s.i.g. (pounds per square inch gauge) may be employed, if desired. With the lighter hydrocarbon reactants, a moderate amount of pressure will promote liquid phase reaction conditions.

It is important that the quantity of tritiated water employed provide a sufficient amount of tritium to effectively convert the hydrocarbon reactant to a tritium-containing or radioactive hydrocarbon. It has been found that the amount of dilute tritiated water having a specific activity within the above range that can be dissolved in the anhydrous hydrocarbon reactant is sufficient to produce the desired radioactive hydrocarbons. Generally, the amount of tritiated water employed should range from about 0.005 to 0.5% by weight based on the weight of the reactants.

In conducting the process of this invention, the hydrocarbon feed stream is first agitated with tritiated water having a radioactivity level within the above range in an amount that is very substantially in excess of the amount necessary to saturate the feed stream or is in a substantial excess of the amount of water already dissolved in the hydrocarbon. The mixing must be quite thorough so that the water ultimately dissolved in the hydrocarbon feed is tritiated water having an adequate amount of radioactivity to transfer to the hydrocarbon being reacted.

When the hydrocarbon has been saturated with the tritiated water, all of the excess water is separated from the reaction mixture. The reaction mixture is introduced into a suitable reaction zone where it is contacted with boron trifluoride and reacted at a temperature within the range of -30° C. to 100° C. for a sufficient time to complete the reaction. Generally, the reaction will be completed in a period ranging from about 1 minute to 1 hour. It will be appreciated that when olefins are employed in the feed $\text{BF}_3\text{-H}_2\text{O}$ catalyst complexes also formed concurrently will promote the formation of olefin polymers.

The following example illustrates the practice of this invention.

Example

A hydrocarbon feed stream consisting of 52 weight percent of liquefied isobutylene and 48 weight percent of pentane was saturated with tritiated water of known specific activity (1.77 microcuries per gram) in an agitated vessel containing a large excess of the tagged water. Thorough contacting was effected so that any untagged water dissolved in the charge would be replaced for all practical purposes and the original untagged water would have a negligible dilution effect on the water dissolved in the charge.

The feed stream was separated from the excess water

3

and was continuously passed into a well agitated reactor operating at 0° F. and 85 p.s.i.g. 0.04% of boron trifluoride was admixed with the feed in the reactor and the reaction was completed in a residence time of one hour. The total amount of radioactivity introduced through the tritiated water amounted to 32.3 mc. (microcuries).

The effluent from the reactor was passed through a fixed-bed adsorber containing silica gel which quantitatively removed the boron trifluoride and the water. Some further reaction and transfer of tritium was found to take place in the adsorber unit, conveniently referred to as a secondary reactor, because of the presence of boron trifluoride. The bulk of the pentane was removed in a continuous flasher at 320° F. and 54 p.s.i.g. and the light polymer then removed in two successive passes through a vacuum evaporator at 10 mm. of mercury absolute with the first pass at 200° F. and the second one at 300° F.

Analysis of the product of the reaction to trace the total radioactivity input showed the following activity balance:

	Mc.
To isobutylene and polymer in the primary reactor	23.0
To pentane in the primary reactor	3.8
To isobutylene and polymer in the secondary reactor	6.9
Activity left in water and silica gel (by difference)	0.0

33.7

As is evident from the above table, all of the radioactivity was accounted for within a 4% margin of error. Substantially all of the radioactivity was transferred to the hydrocarbon reactants. Surprisingly, no radioactivity was found in either the water or in the silica gel bed showing the high efficiency of this process for transferring the tritium to the treated hydrocarbons.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A method for preparing a tritium-containing hydrocarbon which comprises reacting a hydrocarbon with tritiated water having an activity in the range of 0.001 to 1 million microcuries per gram in the presence of a catalyst consisting of boron trifluoride, said hydrocarbon being selected from the group consisting of saturated and unsaturated hydrocarbons having from about 3 to 30 carbon atoms.

4

2. A method according to claim 1 in which said olefin hydrocarbon is isobutylene.

3. A method according to claim 1 in which said saturated hydrocarbon is pentane.

4. A method according to claim 1 in which said reaction is conducted at a temperature in the range of -30° to 100° C.

5. A method for preparing a radioactive hydrocarbon which comprises reacting in mixture of an olefinic hydrocarbon having from about 3 to 30 carbon atoms and a saturated hydrocarbon having from about 3 to 30 carbon atoms with 0.005 to 0.5 weight percent tritiated water having an activity in the range of 0.001 to 1 million microcuries per gram in the presence of 0.01 to 5 weight percent of a catalyst consisting of boron trifluoride.

6. A method according to claim 5 in which said olefin is isobutylene and said saturated hydrocarbon is pentane.

7. A method for preparing a radioactive polyisobutylene and a radioactive paraffin which comprises admixing isobutylene with a paraffin to form a reaction mixture, saturating said mixture with tritiated water having an activity in the range of .001 to 1,000,000 microcuries per gram and reacting said mixture at a temperature in the range of -30 to 100° C. in the presence of 0.01 to 5 weight percent of a catalyst consisting of boron trifluoride.

References Cited by the Examiner

UNITED STATES PATENTS

2,766,312 10/56 Serniuk ----- 260—683.15
3,009,971 11/61 Mottlan ----- 260—676

OTHER REFERENCES

Deuterium Hydrogen Exchange of Some Hydrocarbons on Aluminosilicate Catalyst, by A. Z. Dorogochinskii et al., Akad. Nauk. S.S.S.R., Inst. Fiz. Khim., Soveshchanie, Moscow, 1956, vol. 9, pp. 162-7 (abstracted in Chem. Abstracts, vol. 53, col. 8784f, 1959).

Yavorsky et al.: 7th Quarterly Technical Status Report for November 1, 1960-January 31, 1961," NYO-9141, Feb. 15, 1961 (Consolidation Coal Co., R. & D. Div., Library, Pa.).

Yavorsky et al.: "7th Quarterly Technical Status Report February 1, 1961- . . .," NYO-9142, May 1, 1961 (Consolidation Coal Co., R. & D. Div., Library, Pa.).

ALPHONOSO D. SULLIVAN, *Primary Examiner*.

MILTON STERMAN, PAUL M. COUGHLAN, JR.,
Examiners.

50