

[54] **SELECTIVE HYDROGENATION OF
POLYCYCLIC AROMATIC
HYDROCARBONS USING AS
CATALYST A SULFIDE OF A
PLATINUM GROUP METAL**

[75] Inventors: Roger W. Amidon, New Haven,
Conn., Harold Greenfield, Litch-
field, Conn.

[73] Assignee: Uniroyal, Inc., New York, N.Y.

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[56]

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UNITED STATES PATENTS

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3,422,001	1/1969	Kouwenhover et al.	208/143
3,022,359	2/1962	Wiese et al.	260/667 X
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Primary Examiner—Patrick P. Garvin

Assistant Examiner—P. F. Shaver

Attorney—James J. Long

[57]

ABSTRACT

Polycyclic aromatic hydrocarbons are selectively hydrogenated using a sulfide of a platinum group metal as a catalyst. For example, naphthalene is partially reduced to tetralin by hydrogenation in the presence of platinum sulfide.

14 Claims, No Drawings

SELECTIVE HYDROGENATION OF POLYCYCLIC AROMATIC HYDROCARBONS USING AS CATALYST A SULFIDE OF A PLATINUM GROUP METAL

This invention relates to a method of selectively hydrogenating polycyclic aromatic hydrocarbons.

Hydrogenation is disclosed in such U.S. Pats. Nos. as 1,894,924, 2,635,081, 2,736,689, 2,967,204, 3,183,278, 3,223,652, 3,239,453, 3,239,454, 3,268,608, 3,269,938, 3,285,984, 3,313,859, 3,336,386, 3,397,249, and 3,422,001; see also J.A.C.S., 87, 2767 (1965), Communication to the Editor, "Platinum Metal Sulfides as Heterogeneous Hydrogenation Catalysts" by F. S. Dovell and H. Greenfield; Annals of New York Academy of Sciences, Vol. 145, Article 1, Pages 108-115, Oct. 18, 1967, "Platinum Metal Sulfides in Catalytic Hydrogenations" by Harold Greenfield. However, it has been desired to provide more efficient selective hydrogenation of polycyclic aromatic hydrocarbons to partially reduced polycyclic hydrocarbons, e.g., the conversion of naphthalene to tetralin. The reduction of naphthalene to tetralin is not a new reaction and the sulfides of the base metals, such as molybdenum, nickel and tungsten, have long been used for such transformation, but not the sulfides of platinum metals. Goble (U.S. Pat. No. 3,285,984) teaches the selective hydrogenation of polycyclic aromatics with a platinum catalyst in the presence of a sulfur compound. The recommended temperature is 500° - 900°F. (ca. 260° - 480°C.), preferably 600° - 800°F. (ca. 315° - 425°C.), rather severe conditions. Even at 800°F (427°C.) the conversion of naphthalenic material in Goble is only 71 percent and, because of the severity of the reaction conditions, considerable formation of side products such as alkylbenzenes and dimethylindanes occurs.

The present invention is based on the discovery that the sulfides of the platinum group metals are excellent catalysts for hydrogenation of polycyclic aromatic hydrocarbons. Any platinum group metal sulfides may be employed in the invention, i.e., the sulfides of palladium, osmium, iridium, rhodium and ruthenium, as well as the sulfide of platinum. The preferred catalyst is platinum sulfide, PtS₂, on the basis of activity, selectivity and stability. The method of the invention is applicable to polycyclic aromatic hydrocarbons in general, whether linear or non-linear, including by way of non-limiting example such polycyclic aromatic hydrocarbons as naphthalene, anthracene, indene, acenaphthylene, coumarin, phenanthrene, pyrene, chrysene, perylene, fluoranthene, etc. Included as equivalent to the foregoing are the substituted forms, such as substituted naphthalenes, e.g., 1-methylnaphthalene, 2-methylnaphthalene, other 1 or 2-alkyl substituted naphthalenes where the alkyl group may be ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl, etc., dialkyl substituted naphthalenes, e.g., 1,2-dimethylnaphthalene, 1,3-dimethylnaphthalene, 1,4-dimethylnaphthalene, 1,5-dimethylnaphthalene, etc., and higher substituted alkyl naphthalenes containing up to 8 alkyl groups; similarly substituted naphthalenes where the substituent may be a halogen, alkoxy, aryloxy, carboxy, carboalkoxy, or similar grouping that is unreactive under the reaction conditions, including combinations of such groups. Likewise, any of the other

polynuclear hydrocarbons shown may be substituted by one or more and by any combination of inactive groups in variety.

The invention is practiced by contacting the polycyclic aromatic hydrocarbon with hydrogen and the catalyst. For best results the catalyst is supported or deposited in conventional manner on a solid carrier substance, such as carbon, alumina, silica, clay, or other usual supports or refractory substances (see, for example, U.S. Pat. No. 3,285,984, col. 2, lines 23-42).

The process may be carried out batchwise, for example in an autoclave, or in a continuous system using either tank or pipe-line reactors. The hydrogenation may be effected in the liquid phase using a slurry of catalyst or a fixed catalyst bed. Alternatively the invention may be practiced in the vapor phase with either fluidized or fixed bed catalysts.

In liquid phase hydrogenation it is usually convenient to have an appropriate inert solvent present, such as for example a hydrocarbon, whether aliphatic as in such alkanes as n-hexane, n-octane, etc., cycloaliphatic as in such cycloalkanes as cyclohexane, etc., or aromatic as in benzene, toluene, etc. or a non-hydrocarbon as in such halogenated hydrocarbons as dichlorobenzene, etc., or an alcohol such as the alkanols (e.g., methanol, ethanol, 2-propanol, etc.), ethers, such as diethylether, dibutyl ether, dioxane, glycol diethers, etc; esters, such as ethyl acetate, butyl acetate, 1-ethylhexyl acetate, etc., or any other suitable conventional solvent.

Agitation, elevated temperatures and pressures increase the speed of the hydrogenation. In any specific case the economic optimization of temperature, pressure, catalyst level, feed concentration and cycle time will vary and can be determined by conventional means. It is a remarkable advantage of the invention, in comparison to such prior art as U.S. Pat. No. 3,285,984 for example, that excessively high operating temperatures are not usually required. Temperatures in the range of 80° to 300°C., and hydrogen pressures in the range of 500 to 5000 psig are ordinarily satisfactory, but other temperatures and pressures may be used.

The process of this invention has the great advantage that no sulfur or sulfur-containing compound need be added to the hydrocarbon feed. On the other hand, the present catalysts are remarkably poison resistant and make possible the efficient use of feeds containing sulfur and other poisons that render impractical the use of conventional metal and metallic oxide hydrogenation catalysts.

It is an important advantage of the invention that the platinum group metal sulfides employed as catalysts often effect complete or almost complete selective formation of a single desired product even at complete conversion of the starting material.

The following examples will serve to illustrate the practice of the invention in more detail.

EXAMPLES

Example 1. Reduction of naphthalene to tetralin

A mixture of 125 grams (0.975 mole) of naphthalene, 200 ml. of toluene, and 6.0 grams of 5 percent platinum sulfide on carbon was added to a 600-ml. Magne Dash autoclave. The autoclave was sealed, purged with nitrogen and then with hydrogen, and hydrogen added to a pressure of 1000 psig. The vessel

was heated with agitation for 17.5 hours at 275°–280°C. and 1400–1700 psig. The autoclave was cooled and depressurized, and the reaction product removed. The reaction mixture was filtered through diatomaceous earth to remove the catalyst. A liquid residue of 126 grams remained after the solvent was distilled from the filtrate. This residue was shown by infrared analysis to contain 80 percent of tetralin, and was shown by glpc analysis to contain 81 percent of tetralin, 19 percent naphthalene, and no detectable decalin.

Example 2. Reduction of anthracene to 9,10-dihydroanthracene

A mixture of 35.6 grams (0.20 mole) of anthracene, 220 ml. of 2-propanol, and 2.5 grams of 5 percent platinum sulfide on carbon was added to a 600-ml. Magne Dash autoclave. The autoclave was sealed, purged with nitrogen and then hydrogen, and hydrogen added to a pressure of 1300 psig. The vessel was heated with agitation for 4 hours at 165°C. and 1550–1600 psig. The autoclave was cooled and depressurized, and the reaction product removed. The reaction mixture was filtered through diatomaceous earth to remove the catalyst. The catalyst was washed with hot 2-propanol, and the solvent was removed from the combined filtrate and washings by evaporation on a steam bath. The residue consisted of 34 grams of a solid from which dihydroanthracene melting at 104°–108°C. (lit. value, 108.5°C.) was obtained by recrystallization from 2-propanol.

Example 3. Reduction of indene to indane

A mixture of 65.1 grams (0.56 mole) of indene, 225 ml. of toluene, and 6.0 grams of 5 percent platinum sulfide on carbon was added to a 600-ml. Magne Dash autoclave. The autoclave was sealed, purged with nitrogen and then hydrogen, and hydrogen added to a pressure of 1200 psig. The vessel was heated with agitation at 120°C. and 1200–1400 psig for 1 hour, at which time the reaction stopped abruptly after a hydrogen absorption of about 0.55 mole (98 percent of theory). The autoclave was cooled and depressurized and the reaction product removed. The reaction mixture was filtered through diatomaceous earth to remove the catalyst. The solvent was evaporated from the filtrate in a rotary evaporator under reduced pressure. The liquid residue was shown by glpc and infrared spectroscopy to be identical with an authentic sample of indane.

Example 4. Reduction of acenaphthylene to acenaphthene

A mixture of 85.2 grams (0.56 mole) of acenaphthylene, 200 ml. of toluene, and 6.0 grams of 5 percent platinum sulfide on carbon was added to a 600-ml. Magne Dash autoclave. The autoclave was sealed, purged with nitrogen and then hydrogen, and hydrogen added to a pressure of 1200 psig. The vessel was heated with agitation at 100°–140°C. and 1000–1300 psig for 20 minutes, at which time gas absorption stopped abruptly. The autoclave was cooled and depressurized, and the reaction product removed. The reaction mixture was filtered through diatomaceous earth to remove the catalyst. The solvent was evaporated from the filtrate in a rotary evaporator under reduced pressure. The residue consisted of 82 grams (95 percent yield) of a solid that was shown by glpc to consist of a single component identical with an authentic sample of acenaphthene.

Example 5. Reduction of coumarin to dihydrocoumarin

A mixture of 43.8 grams (0.30 mole) of coumarin, 115 ml. of benzene, and 3.3 grams of 5 percent platinum sulfide on carbon was added to a 265-ml. Magne Dash autoclave. The autoclave was sealed, purged with nitrogen and then hydrogen, and hydrogen added to a pressure of 700 psig. The vessel was heated with agitation for 5.5 hours at 190°C. and 600–900 psig. The hydrogen absorption was about 0.3 mole (100 percent of theory). The autoclave was cooled and depressurized, and the reaction product removed. The reaction mixture was filtered through diatomaceous earth to remove the catalyst. The solvent was evaporated from the filtrate on a steam bath. The residue was shown by glpc to be identical with an authentic sample of dihydrocoumarin.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A method of selectively hydrogenating a polycyclic aromatic hydrocarbon comprising contacting said polycyclic hydrocarbon with hydrogen in the presence of a catalyst consisting of platinum sulfide.

2. A method of selectively partially hydrogenating a polycyclic aromatic hydrocarbon comprising contacting said polycyclic aromatic hydrocarbon with hydrogen in the presence of a catalyst consisting of platinum sulfide, the said polycyclic aromatic hydrocarbon being selected from the group consisting of naphthalene, anthracene, indene, acenaphthalene, and coumarin, to produce a partially hydrogenated product selected from the group consisting of, respectively, tetralin, 9,10-dihydroanthracene, indane, acenaphthene and dihydrocoumarin.

3. A method as in claim 2 carried out at a hydrogen pressure of 500 to 5000 psig.

4. A method as in claim 2 carried out at a temperature of 80° to 300°C.

5. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is dissolved in an inert solvent.

6. A method as in claim 2 in which the said catalyst is deposited on a solid carrier.

7. A method as in claim 6 in which the said carrier is carbon.

8. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is naphthalene and the hydrogenation product is tetralin.

9. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is anthracene and the hydrogenation product thereof is 9,10-dihydroanthracene.

10. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is indene and the hydrogenation product thereof is indane.

11. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is acenaphthylene and the hydrogenation product thereof is acenaphthene.

12. A method as in claim 2 in which the said polycyclic aromatic hydrocarbon is coumarin and the hydrogenation product thereof is dihydrocoumarin.

13. A method as in claim 2 in which said polycyclic aromatic hydrocarbon is agitated in an inert solvent in the presence of hydrogen under pressure and the said catalyst is deposited on a carrier.

14. A method as in claim 13 in which the polycyclic aromatic hydrocarbon is naphthalene and the hydrogenation product thereof is tetralin.

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