

1

2,807,647

PRODUCTION OF UNSATURATED CARBONYLIC COMPOUNDS

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This invention relates to the production of alpha,beta-unsaturated carbonylic compounds by controlled catalytic oxidation of paraffinic hydrocarbons having at least three carbon atoms to the molecule. The invention relates more particularly to the production of alpha-methylene aldehydes by the oxidation of paraffinic hydrocarbons having at least three carbon atoms to the molecule. A particular aspect of the invention relates to the production of acrolein by the controlled catalytic oxidation of normally gaseous hydrocarbons comprising propane.

Alpha,beta-unsaturated carbonylic compounds such as the alpha,beta-unsaturated aliphatic aldehydes and ketones, for example, acrolein, are of value as starting and intermediate materials in the production of valuable chemical products. Methods directed to the conversion of olefins to alpha,beta-unsaturated carbonylic compounds comprising unsaturated aliphatic aldehydes have been disclosed heretofore. The method described and claimed in U. S. Patent 2,451,485, enables the efficient conversion of alpha-olefins of three or more carbon atoms to oxidation products consisting predominantly of alpha,beta-unsaturated carbonylic compounds by the use of a specific catalyst under specific operating conditions. In accordance with the patented process propylene is readily converted to alpha,beta-unsaturated carbonylic compounds comprising acrolein. Such processes are limited to the efficient conversion of only the olefin content of the charge to these desired unsaturated carbonylic compounds. Processes disclosed heretofore directed to the oxidation of paraffins are generally limited to the production of oxidation products wherein the alpha,beta-unsaturated carbonylics, if present at all, are present in such low concentrations and in mixtures of such complexity of composition that their recovery therefrom is generally economically unfeasible. In view of the substantial amounts of readily available paraffins, and the potential value of the alpha,beta-unsaturated carbonylics, a process bringing within the realm of practicability the efficient conversion of paraffinic hydrocarbons to alpha,beta-unsaturated carbonylic compounds is greatly desired.

It is an object of the present invention to provide an improved process enabling the more efficient conversion, by controlled catalytic incomplete oxidation, of paraffinic hydrocarbon to oxidation products comprising alpha,beta-unsaturated carbonylic compounds.

Another object of the invention is the provision of an improved process enabling the more efficient conversion of open chain paraffinic hydrocarbons having at least three carbon atoms to the molecule to oxidation products comprising alpha,beta-unsaturated aldehydes and ketones containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is directly linked to the carbon atom of the carbonyl group.

Still another object of the invention is the provision of an improved process enabling the more efficient conversion of normally gaseous paraffinic hydrocarbons having at least three carbon atoms to the molecule to oxidation

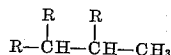
2

products comprising alpha-methylene aldehydes corresponding to said paraffinic hydrocarbons.

A specific object of the invention is the provision of an improved process enabling the more efficient conversion of normally gaseous hydrocarbons comprising propane to oxidation products comprising acrolein. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the present invention, unsaturated carbonylic compounds containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, are obtained by contacting a paraffinic hydrocarbon having at least three carbon atoms in admixture with oxygen with a solid cuprous oxide catalyst, at an elevated temperature, in the presence of an added promoter comprising sulfur. In accordance with the process of the invention alpha,beta-unsaturated carbonylic compounds comprising acrolein are obtained by contacting paraffinic hydrocarbons comprising propane in admixture with oxygen with a solid cuprous oxide catalyst at an elevated temperature in the presence of a promoter containing sulfur as the essential active component.

Hydrocarbons converted by controlled incomplete catalytic oxidation to oxidation products comprising alpha,beta-unsaturated carbonylic compounds in accordance with the present invention are the paraffin hydrocarbons having at least three carbon atoms to the molecule represented by the formula:



wherein each R is the same or a different member of the group consisting of hydrogen, alkyl and cycloalkyl radicals, and wherein any two of the R's may represent alkyl groups linked by carbon-to-carbon bond to form a closed ring structure. The paraffins employed as charge to the process may be defined as the paraffinic hydrocarbons having a saturated aliphatic hydrocarbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group, and the other two each have a hydrogen atom directly attached thereto.

Examples of such suitable paraffinic hydrocarbons are the open chain paraffinic hydrocarbons such as propane, n-butane, isobutane, n-pentane, 2-methyl butane, n-hexane, 2,3-dimethyl butane, n-heptane, 2,3-trimethyl butane, 2,2-dimethyl pentane, n-octane, 2,2,3,3-tetramethyl butane, etc.; the alkyl-substituted cycloparaffins such as, for example, methyl cyclopropane, methyl cyclobutane, methyl cyclopentane, methyl cyclohexane, ethyl cyclopentane, dimethyl cyclopentane, and higher homologues thereof, etc. These suitable compounds may be further substituted in various degrees by heterocyclic radicals. The charge to the process of the invention need not necessarily consist of a single paraffinic hydrocarbon, but may comprise one or more paraffinic hydrocarbons of the above-identified class. Suitable charge to the process of the invention comprises the hydrocarbon fractions obtained in conventional refinery operations comprising one or more paraffinic hydrocarbons of the above-identified class. Such hydrocarbon fractions comprise, for example, the propane, butane, pentane, etc., fractions obtained by fractionation of mixtures of petroleum hydrocarbons of natural or synthetic origin, or of the products of conventional refinery operations such as hydrogenation, reforming, cracking etc.

The oxygen employed in converting paraffins of the above-identified class to alpha,beta-unsaturated carbonylic compounds in accordance with the invention, may be obtained from any suitable source. The oxygen may be employed as such, in relatively pure state, or

in the form of an oxygen-containing gas such as, for example, air.

The ratio of oxygen to paraffin charged to the process may vary considerably within the scope of the invention. In general the paraffin is added in substantial excess over the stoichiometrical amount; the maximum amount of oxygen tolerated being defined by the explosive limit under the specific operating conditions employed. Mole ratios of paraffin to oxygen in the range of from about 1:1 to about 8:1 generally give satisfactory results. Higher ratios, for example, up to a mole ratio of paraffin hydrocarbon to oxygen of about 30:1 are often advantageously employed.

Essential to the attainment of the controlled catalytic incomplete paraffin oxidation is the use of a catalyst comprising copper in the form of cuprous oxide as the essential active ingredient. Suitable catalysts comprise those consisting essentially of the cuprous oxide in combination with a suitable solid catalyst support material. Suitable carrier materials comprise, for example, silica gel, activated alumina, bauxite, Porocel, Alundum, diatomaceous earth, silicon carbide, silicon carbide aggregate, Carborundum, pumice, charcoal, etc. Adsorptive materials, such as, for example, adsorptive alumina, fullers earth, etc., are comprised in the suitable support materials. A particularly suitable catalyst for use in the process of the invention comprises one consisting essentially of cuprous oxide in admixture with an aluminous material such as, for example, Aloxite. The concentration of copper in the catalyst may vary considerably within the scope of the invention. Thus, the copper content of the catalyst plus support may range, for example, from about 0.5% to about 25% and preferably from about 5 to about 15% by weight calculated as metallic copper. Higher or lower proportions of copper may, however, be employed within the scope of the invention. Suitable copper-containing catalysts may be obtained by impregnating a support material with a solution of a copper compound such as, for example, cupric nitrate or chloride, or with an ammonium compound comprising copper, for example, copper ammonium nitrate. The impregnated support is subjected to conditions resulting in the decomposition of at least a substantial part of the deposited copper compound with the formation of cupric oxide, for example, by subjection to a temperature in the range of from about 250 to about 400° C. in an oxygen-containing atmosphere. Thereafter the cupric oxide content of the catalyst is converted to cuprous oxide in a reducing atmosphere. The invention is in no wise limited to the use of cuprous oxide catalysts produced by any specific method. Suitable cuprous oxide-containing catalysts may be prepared by methods described in the prior art.

Normally gaseous materials, or materials which are vapors under the conditions of execution of the controlled oxidation, which are relatively inert, may be employed as diluents. Such diluent materials comprise, for example, nitrogen, steam, normally gaseous olefins, methane, etc. One or more such diluents may be employed to aid in maintaining desired operating conditions. They may be employed, for example, to aid in maintaining optimum temperature conditions, to introduce promoters into the reaction zone, etc. It is to be pointed out, however, that an important advantage of the invention resides in the ability to effect the desired controlled paraffin oxidation in the absence of any substantial amounts of added diluents, such as, for example, steam. The substantial reduction in the volume of materials passed through the process in thus omitting substantial amounts of diluents, such as steam, represents a considerable saving in cost of initial installation as well as operation of the process.

The controlled incomplete oxidation of the paraffins is carried out at an elevated temperature in the range of, for example, from about 200° to about 600° C. and

preferably from about 250 to about 450° C. The temperature used depends primarily upon the catalyst, the particular paraffin being treated, and the correlated conditions of the rate of throughput or contact time, and the ratio of paraffin to oxygen. Apparent contact times of from about 0.1 sec. to about 10 sec. generally are satisfactory. The apparent contact time may be defined as the length of time in seconds a unit volume of gas measured under the conditions of reaction is in contact with a unit apparent volume of the catalyst. It may be calculated, for example, from the apparent volume of the catalyst bed, the average temperature of the catalyst, the pressure (if different from atmospheric), and the flow rates of the several components of the reaction mixture. The controlled oxidation may be carried out at subatmospheric, atmospheric or superatmospheric pressures. Pressures in the range of from about atmospheric to about 1000 pounds per square inch (gauge) and preferably from about atmospheric to about 250 p. s. i. g. are satisfactory.

Essential to the attainment of the objects of the invention is the presence in the reaction zone of a promoter comprising sulfur as the active component. Sulfur employed as promoter may be introduced into the reaction zone as elementary sulfur or in the form of a sulfur-containing compound of organic or inorganic character. Sulfur compounds which may be employed as promoters in the process of the invention comprise, for example, elementary sulfur; organic sulfur compounds, such as carbon disulfide, carbonyl sulfide (COS); mercaptans, such as methyl mercaptan, ethyl mercaptan, propyl mercaptan, butyl mercaptan, etc.; mercaptals, mercaptols; heterocyclic organic sulfur compounds, such as thiophene, thionaphthenes, dibenzothiophenes, dinaphthothiophene, thioaldehydes, polymeric thioaldehydes; thiophenols, such as, thiophenol, paramethyl thiophenol, ethyl thiophenol, thiohydroquinone; thioorganic acids, such as thiopropionic acid and homologues of such organic sulfur compounds; inorganic sulfur compounds, such as, for example, hydrogen sulfide, sulfur dioxide, sulfur trioxide, sodium thiosulfate, potassium thiosulfate, sodium sulfide, potassium sulfide, calcium sulfide, etc.

Preferred promoters comprise the normally gaseous sulfur compounds and the organic sulfur compounds having a relatively low boiling temperature. Such preferred promoters comprise, for example, carbonyl sulfide, carbon disulfide, hydrogen sulfide, methyl mercaptan, etc.

The sulfur compounds are effective in their ability to render the cuprous oxide catalyst active for the controlled incomplete paraffin oxidation when present in relatively small amount. Thus, whereas in their complete absence no substantial production of the desired alpha,beta-carbonylic compounds is generally obtained, their presence in an amount as low as, for example, about 50 p. p. m., by weight calculated as elementary sulfur and based on the paraffin content of the feed is generally sufficient to result in substantial conversion of the paraffinic charge to the desired saturated carbonylic compounds. The amount of sulfur promoter preferably employed may vary considerably within the scope of the invention. The optimum amount will generally depend to some degree upon the specific sulfur-containing compound used as promoter and the specific operating conditions employed. In general an amount of sulfur promoter providing an amount of sulfur in the range of, for example, from about 0.001 to about 1.000, and preferably from about 0.005 to about 0.05% by weight, calculated as elementary sulfur and based upon the paraffin content of the charge, will be found satisfactory. Greater or lesser concentrations of the promoter may, however, be employed within the scope of the invention.

The process of the invention may be carried out in batch, semi-continuous or continuous operation. Any suitable reactor enabling efficient contact of reactants with the catalyst may be employed within the scope of the in-

vention. The cuprous oxide catalyst may be employed in the form of a stationary or fixed bed of solid supported cuprous oxide or in the form of a fluidized bed consisting essentially of cuprous oxide without support material.

The invention is in no wise limited to any specific method for introducing the sulfur promoter into the reaction zone. Thus, the sulfur promoter may be added to either the paraffinic charge or the oxygen charge to the reaction zone, or to both. At least a part or all of the promoter may be separately introduced into the reaction zone. Preferred methods for introducing the promoter into the reaction zone will vary to some extent in accordance with the specific sulfur promoter employed. Thus, the promoter may be introduced into the reaction zone as a solution, suspension, a dust, vapor, smoke, etc. It may be introduced into the reaction zone as a separate stream as such, or in a suitable carrying medium. Suitable carrying media comprise, for example, liquids or gases which are inert under the conditions of executing the reaction. Control of the amount of promoter introduced into the reaction zone can in certain cases be attained by passage of a portion of the charge, or a suitable gaseous or liquid carrying medium, through a promoter-laden pick-up vessel under controlled conditions of temperature and pressure and then into the reaction zone. Comprised within the scope of the invention is the inclusion of sulfur or a sulfur compound such as, for example, a metal sulfide in relatively small amounts, in the catalyst during its manufacture. Sulfides which may thus be included in the catalyst bed comprise the solid inorganic sulfides, such as sulfides of metals of groups I, VI, VII and VIII of the periodic tables of the elements, comprising, for example, the sulfides as As, Cu, Fe, Co, Ni, W, etc. The sulfides thus incorporated in the catalyst before use are added only in promotional amounts, that is, in amounts generally not exceeding about 1.0% by weight of the cuprous oxide content of the catalyst.

Under the above-defined conditions the paraffinic hydrocarbons of the above-defined class are converted to oxidation products comprising unsaturated carbonylic compound containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is directly linked to the carbon atom of the carbonyl group. Thus, conversion of paraffinic hydrocarbons having from three to four carbon atoms to the molecule to the corresponding alpha,beta-unsaturated aldehydes, having from three to four carbon atoms to the molecule, such as, for example, the conversion of propane to acrolein, is readily obtained. The efficiency with which the paraffins are converted to oxidation products consisting essentially of alpha,beta-unsaturated carbonylic compounds, in accordance with the invention as a result of the presence of the sulfur promoter, is evidenced by the following example.

Example I

In an operation identified as run A, a mixture consisting of 70 mol percent propane and 30 mol percent air was passed through a bed of cuprous oxide catalyst comprising 2.2% by weight of copper in the form of cuprous oxide supported upon an Aloxite support, at a temperature of 450° C., a pressure of 75 pounds per square inch (gauge), and a contact time of 0.2 second.

In two separate operations, identified as runs B and C, respectively, propane was subjected to controlled catalytic oxidation under substantially identical conditions employed in run A with the exception that carbon disulfide was added to the charge to the reaction. The carbon disulfide was added to the charge in an amount equal to 60 parts per million by weight of propane in the charge in run B, and 180 parts per million by weight of propane in the charge in run C.

Results obtained in each of the operations A, B and C in terms of the percentage conversion of propane and oxygen, and in terms of the percentage yields of oxygenated products based on the propane which reacts, are set forth in the following table:

TABLE A

Runs.....	A	B	C	D
Promoter.....	None	CS ₂	CS ₂	CS ₂ (50 p. p. m.)
Yields on propane reacted to oxygenated products:				
Acrolein.....	1	39	58	40
Saturated carbonylics calculated as acetaldehyde.....	7	11	4	3
CO.....	16	32	24	23
CO ₂	75	14	10	32
Alcohols calculated as methanol.....	1	4	4	2
Oxygen conversion.....	49	19	25	48
Propane conversion.....	1.3	0.7	1.6	3.1

The effect of the sulfur, it is to be pointed out, is selective with respect to the paraffinic component of the charge. Whereas its presence makes possible the conversion of the paraffin charge to corresponding alpha,beta-unsaturated carbonylic compounds under the conditions of the invention, it suppresses any substantial oxidation of olefinic hydrocarbons to these products under otherwise substantially identical conditions. As shown by the following example, in the absence of the sulfur compound olefinic hydrocarbons, such as, for example, propylene, are converted to unsaturated carbonylic compounds. Introduction of sulfur into the catalyst bed, however, results in suppressing formation to any substantial degree of the desired alpha,beta-unsaturated carbonylic compounds.

Example II

Propylene was subjected to controlled catalytic oxidation by passing a mixture consisting of 22 mol percent propylene, 4 mol percent oxygen, 16 mol percent nitrogen, and 58 mol percent water (steam) through a bed of cuprous oxide catalyst consisting essentially of 2% by weight of copper in the form of cuprous oxide supported on Aloxite, at a temperature of 470° C., a pressure of 75 pounds per square inch (gauge), and a contact time of 0.2 seconds. A 75% conversion based on oxygen charged was obtained with an acrolein yield of 59% based on the propylene reacted.

The operation was terminated after 36 hours of operation and the catalyst bed was treated by passing propylene therethrough containing 0.005% of carbonyl sulfide at a temperature of 500° C. for a period of 4 hours.

Resumption of the propylene oxidation under conditions substantially identical to those employed before the catalyst treatment with carbonyl sulfide-containing propylene resulted in an oxygen conversion of less than 10% but with an acrolein yield of less than 10%.

In the presence of a sulfur promoter, propylene becomes substantially inert under the conditions of execution of the controlled paraffin oxidation of the invention. Its presence therefore in no wise affects the ability of the sulfur-promoted cuprous oxide catalyst to convert paraffins to alpha,beta-unsaturated carbonylic products. Propylene may thus be tolerated as a contaminant of the paraffinic charge to the process, or may even be employed as inert diluent, or as a carrier for the sulfur promoter. The selective inert state of propylene in the process of the invention is illustrated by the following example:

Example III

A mixture having the following composition

	Mol percent
Propane	58
Oxygen (as air).....	4
Propylene	22
Nitrogen	16

was passed through a bed of cuprous oxide catalyst consisting of 2% of copper in the form of cuprous oxide supported on Aloxite, at 420° C., a pressure of 75 pounds

per square inch (gauge) and a contact time of 0.2 seconds. Carbonyl sulfide (COS) was added to the charge to the reaction in an amount equal to 50 parts per million (by weight) based upon the propane content of the charge. A 70% conversion of oxygen and a 2.1% conversion of propane, were obtained with an acrolein yield of 44% based on the propane reacted to oxygenated products.

It is seen from the foregoing example that the presence of propylene in the paraffin charge does not reduce the ability of the sulfur promoted catalyst to convert propane to acrolein. Furthermore, not only is there no olefin consumption in the reaction, but there is occasioned a net increase in olefin during the course of the operation.

The effect of the sulfur promoter upon the cuprous oxide catalyst is lasting. The sulfur promoter need be introduced into the reaction zone only periodically or intermittently during the course of the operation. It is possible to obtain the promotional effect of the sulfur upon the cuprous oxide by pretreating the catalyst with a sulfur promoter prior to initiating the oxidation reaction. The catalyst bed may be activated for the controlled paraffin oxidation, for example, by passing a hydrocarbon stream containing a sulfur promoter there-through at a temperature approximating the oxidation reaction temperature. Temperatures somewhat lower than, approximating, or exceeding, the paraffin oxidation temperatures may be employed in thus activating the catalyst. Suitable carrying media for the sulfur promoter during such preactivation comprise normally gaseous materials, or normally liquid materials which are vapors under the conditions of the preactivation. Suitable carrying media comprise, for example, paraffinic hydrocarbons such as methane, ethane, propane, butane, etc.; olefinic hydrocarbons such as, for example, ethylene, propylene butylene, etc.; inert gases such as nitrogen, etc. Suitable methods for preactivating the catalyst comprise the passage therethrough of sulfur-containing refinery fractions, such as hydrogen sulfide, and/or mercaptan-containing normally gaseous hydrocarbon fractions, and the like. The ability to thus preactivate the catalyst by contact with a sulfur-containing compound prior to the paraffin oxidation is evidenced by the following example:

Example IV

A sulfur-free mixture containing 70 mol percent propane, 6 mol percent oxygen, 24 mol percent nitrogen, and 0.3 mol percent ethane, was passed over a cuprous oxide catalyst at a temperature of 449° C., a pressure of 75 pounds per square inch (gauge), and a contact time of 0.2 second. The catalyst employed was the cuprous oxide catalyst which had been used in the operation of the foregoing Example III wherein the charge to the reaction contained carbonyl sulfide. A 37% conversion of oxygen and 3.1% conversion of propane were obtained with the following yields:

Yields on propane reacted:	Mol percent
Acrolein -----	22
Saturated carbonylics -----	4
CO -----	18
CO ₂ -----	18
Alcohols -----	3
Propylene -----	55

From the foregoing Example IV it is apparent that a substantial amount of propylene was actually formed during the paraffin oxidation reaction. The relatively inert state of olefins, such as propylene, during the paraffin oxidation in the presence of a catalyst preactivated by contact with sulfur is further evidenced by the following example:

Example V

The controlled catalytic oxidation of propane, using a cuprous oxide catalyst which had been pretreated with

carbonyl sulfide, as set forth above under Example IV, was repeated under substantially identical conditions with the exception that a sulfur-free charge containing a small amount of propylene and ethylene and some ethane was employed as feed. The propylene-ethylene-containing feed employed in this operation had the following composition:

	Mol percent
Propane -----	63
Oxygen (as air) -----	6.2
Propylene+ethylene -----	1.6
Ethane -----	3.3

A 34% conversion of oxygen and a 2.6% conversion of propane was obtained with the following yields:

Yields on propane reacted:	Mol percent
Acrolein -----	35
Saturated carbonylics -----	5
CO -----	8
CO ₂ -----	7
Alcohols -----	7
Propylene -----	38

It is apparent from the foregoing Example V that not only is the propylene content of the charge passed through the reactor without any substantial amount thereof being affected but that a net increase in propylene content has taken place.

Activation of cuprous oxide catalyst which has become at least partly spent in the paraffin oxidation reaction is brought about by contacting the spent catalyst with a sulfur compound substantially under the conditions prescribed for preactivation of the catalyst.

A significant advantage of the lasting effect of the sulfur promoters upon the cuprous oxide resides in the ability to activate the catalyst in a zone outside of the reaction zone when employing the cuprous oxide in the fluidized state, thereby avoiding the introduction of any substantial amounts of sulfur promoter into the reaction zone proper. This is of particular advantage in cases where it is desirable to maintain to an absolute minimum the sulfur content of the resulting oxidation products.

Unsaturated carbonylics are recovered from the total oxidation products by conventional means comprising, for example, one or more such steps as quenching by direct contact with a liquid cooling medium such as, for example, a hydrocarbon, water, and the like; scrubbing with water, hydrocarbons, etc.; distillation; extractive distillation; solvent extraction; and the like.

The invention claimed is:

1. The process for the production of unsaturated carbonylic compounds containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, which comprises contacting a paraffinic hydrocarbon having a saturated aliphatic hydrocarbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C. in the presence of a promoting amount of sulfur.

2. The process for the production of unsaturated carbonylic compounds containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, which comprises contacting a paraffinic hydrocarbon having a saturated aliphatic hydrocarbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C.

in the presence of a promoting amount of a sulfur compound.

3. The process in accordance with claim 2 wherein said sulfur compound is carbon disulfide.

4. The process for the production of unsaturated carbonylic compounds containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, which comprises contacting a paraffinic hydrocarbon having a saturated aliphatic hydrocarbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 250 to about 400° C. in the presence of a promoting amount of carbonyl sulfide.

5. The process for the production of unsaturated carbonylic compounds having from three to four carbon atoms to the molecule containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, which comprises contacting paraffinic hydrocarbons comprising paraffins having from three to four carbon atoms to the molecule having a saturated aliphatic carbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst in the presence of a promoting amount of sulfur at a temperature in the range of from about 250 to about 450° C.

6. The process for the production of unsaturated carbonylic compounds having from three to four carbon atoms to the molecule containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group which comprises contacting paraffinic hydrocarbons comprising paraffins having from three to four carbon atoms to the molecule having a saturated aliphatic carbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst in the presence of a promoting amount of a sulfur compound at a temperature in the range of from about 250 to about 450° C.

7. The process in accordance with claim 6 wherein said sulfur compound is carbon disulfide.

8. The process in accordance with claim 6 wherein said sulfur compound is carbonyl sulfide.

9. The process for the production of acrolein which comprises contacting normally gaseous hydrocarbons comprising propane in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C. in the presence of a promoting amount of elementary sulfur.

10. The process for the production of acrolein which comprises contacting normally gaseous hydrocarbons comprising propane in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C. in the presence of an amount of sulfur compound equal to from about 0.001 to about 1.000% by weight calculated as elementary sulfur based upon the propane content of the charge to the reaction.

11. The process in accordance with claim 10 wherein said sulfur compound is carbon disulfide.

12. The process for the production of acrolein which comprises contacting normally gaseous paraffinic hydrocarbons comprising propane in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C. in the presence of a promoting amount of a normally gaseous sulfur compound.

13. A process for the production of acrolein which comprises contacting normally gaseous paraffinic hydrocarbons comprising propane in admixture with oxygen with a solid cuprous oxide catalyst at a temperature of from about 250 to about 450° C. in the presence of an amount of carbonyl sulfide in the range of from about 0.001 to about 0.05% by weight based upon propane in the charge.

14. The process for the production of unsaturated carbonylic compounds containing an olefinic linkage between two carbon atoms of aliphatic character, one of which is linked directly to the carbon atom of the carbonyl group, which comprises contacting a paraffinic hydrocarbon having a saturated aliphatic hydrocarbon chain containing three consecutive carbon atoms, one of which is the carbon atom of an unsubstituted methyl group and each of the other two saturated carbon atoms has a hydrogen atom directly attached thereto, in admixture with oxygen with a solid cuprous oxide catalyst at a temperature in the range of from about 200 to about 600° C. in the presence of a promoting amount of a promoter containing sulfur as the essential active component.

References Cited in the file of this patent

UNITED STATES PATENTS

2,309,718	Thacker	Feb. 2, 1943
2,670,381	Hadley et al.	Feb. 23, 1954