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3,082,273

PROCESS FOR THE PRODUCTION OF UNSATURATED HYDROCARBONS WITH THREE CARBON ATOMS

Hendricus Gerardus Peer, Rijswijk Z-H, and Otto Ernst van Lohuizen, Arnhem, Netherlands, assignors to Nederlandse Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek ten Behoeve van Nijverheid, Handel en Verkeer, The Hague, Netherlands
No Drawing. Filed Nov. 22, 1960, Ser. No. 70,939
Claims priority, application Great Britain Dec. 4, 1959
5 Claims. (Cl. 260-683)

This invention relates to a process for the production of unsaturated hydrocarbons with three carbon atoms. Three such compounds exist, namely allene, otherwise propadiene ($\text{CH}_2=\text{C}=\text{CH}_2$), propyne ($\text{CH}_3-\text{C}\equiv\text{CH}$) and propene ($\text{CH}_2=\text{CH}-\text{CH}_3$); the first and second of these compounds are of great technical importance.

The process according to the invention comprises subjecting isobutene, otherwise isobutylene



to temperatures in excess of 700° C. for a period of less than 1 second at substantially and essentially atmospheric pressures in the absence of diluent gases such as steam, flue gas and the like.

The starting material need not be chemically pure isobutene, but may be a commercial product which mainly consists of isobutene. In this sense the term "isobutene" in the specification and the claims should be understood.

Cracking may be carried out in any conventional way, for example by using pyrolysis tubes or coils made of quartz or stainless steel which may contain filling bodies such as pumice, or by using brick checkerwork or stoves of the type commonly used for carrying out pyrolysis reactions.

It is desirable that the gas obtained after the cracking be cooled quickly, for instance by passing it through a cooling chamber or by quenching it with cold water.

Besides propadiene or a mixture of propadiene and propyne methane is always formed. Under certain conditions other products may also be formed, but it is possible so to choose the cracking conditions that these by-products are only produced in small and even negligible amounts.

The non-converted isobutene can be recycled to the cracking zone.

The isolation of the propadiene and/or propyne by removal of the methane, and of the non-converted isobutene and other products, if present, and the separation of the propadiene and propyne may be effected in any conventional way, for example by cooling and fractional distillation or by adsorption methods.

The following tables are records of experiments showing the influence of contact time and temperature on the cracking of isobutene. The pressure in the cracking zone is essentially atmospheric pressure. The experiments are carried out by passing the isobutene through a quartz tube. The tube is heated to the desired temperature by means of a tube oven. The contact time is controlled by the rate of flow of the isobutene. The resultant mixture is subjected to analysis by means of infra-red spectrography and the results are confirmed by gas chromatography. In the experiments recorded in the tables, those substances which are still volatile at

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minus 180° C. such as methane, have been as far as possible removed from the mixture obtained in the process by cooling the mixture prior to analysis to minus 180° C.

In each experiment the data denotes the percentage by volume of the substance referred to in terms of the total volume of the mixture. The sign "—" denotes that no amount can be found; the sign *t* means that the amount is less than 1% by volume; the sign *s* means that the amount is between 1 and 3% by volume; the sign *m* means that a substantial amount is present.

Table I

[Contact time 0.2 second]

Temperature, ° C.....	750	800	850
isobutene.....	94	89	75
propadiene.....	1	2.2	4
propyne.....	—	—	—
ethene.....	<i>t</i>	<i>s</i>	13.4 (<i>m</i>)
ethyne.....	—	—	—
methane.....	<i>s</i>	—	—
benzene.....	—	<i>t</i>	<i>s</i>

Table II

[Contact time 0.1 second]

Temperature, ° C.....	800	825	850	875
isobutene.....	94	88	82	65
propadiene.....	1.5	2.7	4.2	4.5
propyne.....	—	—	1.5	3
ethene.....	<i>t</i>	1.5	4.2	7.7
ethyne.....	<i>t</i>	<i>t</i>	<i>t</i>	<i>s</i>
methane.....	—	—	—	—
benzene.....	<i>t</i>	<i>t</i>	<i>t</i>	<i>s</i>

Table III

[Contact time 0.05 second]

Temperature, ° C.....	825 ¹	850 ¹
isobutene.....	90	81
propadiene.....	3	4.2
propyne.....	0.3	2
ethene.....	—	0.8
ethyne.....	—	—
benzene.....	0.5	1.1

¹ In these experiments the infra-red spectrography indicates that not all the methane has been removed. A very small amount of propene is also found.

Table IV

[Contact time 0.02 second]

Temperature, ° C.....	900	925	950	975
isobutene.....	98.4	94	88.5	81±4
propadiene.....	1.0	3.3	5.2	6.8
propyne.....	—	0.5	1.8	3.9
propene.....	0.4	1.6	3.2	6.3
ethane.....	—	<i>t</i>	0.4	1.8
ethene.....	<i>t</i>	<i>t</i>	0.4	0.4
ethyne.....	—	<i>t</i>	—	0.4
butadiene.....	—	—	<i>t</i>	0.8
butene.....	—	—	—	—
benzene.....	—	<i>t</i>	0.8	1.5

If to the initial feed of isobutene a gaseous catalyst is admixed, results may be somewhat improved. In Tables V and VI below results are recorded of experiments with azomethane admixed to the isobutene. The percentage of azomethane is for Table V 3 percent by volume on the volume of initial isobutene; in Table VI it is 8 percent by volume on the volume of initial isobutene.

Table V

[Contact time 0.02 second—3% by volume of azomethane]

Temperature, °C.....	875	900	925	950
isobutene.....	96	94.5	90	80
propadiene.....	2.0	3.0	4.1	6.5
propyne.....	t	0.5	1.5	3.2
propene.....	1.0	1.9	2.7	5.8
ethane.....	t	0.4	0.6	2.1
ethene.....	t	t	t	0.6
ethyne.....	—	t	t	0.4
butadiene.....	—	0.4	0.5	0.6
butene.....	—	—	—	—
benzene.....	—	t	—	1.5

Table VI

[Contact time 0.02 second—8% by volume of azomethane]

Temperature, °C.....	850	875	900	925
isobutene.....	92	89	81	78
propadiene.....	3	4.2	5.1	5.9
propyne.....	0.6	1.2	1.8	2.9
propene.....	2.1	3.1	4.2	5.4
ethane.....	0.7	1.0	1.5	2.4
ethene.....	1.3	1.3	1.4	2.1
ethyne.....	0.5	0.1	0.1	0.3
butadiene.....	0.3	0.4	0.6	—
butene.....	—	—	4.0	3.2
benzene.....	t	t	1.0	1.0

In Tables VII and VII are recorded the results, obtained with a contact time of 0.01 second and (Table VII) without azomethane and (Table VIII) with 2 percent by volume of azomethane on the volume of initial isobutene, respectively.

Table VII

[Contact time 0.01 second]

Temperature, °C.....	950	975	1,025	1,050
isobutene.....	98.2	96.5	87.5	81
propadiene.....	0.5	1.9	5.4	7
propyne.....	—	0.3	2.1	3.5
propene.....	0.2	0.7	3.3	5.6
ethane.....	—	0.7	0.7	1.2
ethene.....	—	—	t	0.2
ethyne.....	—	—	t	0.5
butadiene.....	1.2	—	—	—
benzene.....	—	—	0.5	1.5

Table VIII

[Contact time 0.01 second—2% by volume of azomethane]

Temperature, °C.....	950	975	1,000
isobutene.....	97	94	90
propadiene.....	1.7	2.8	4.5
propyne.....	0.3	1.2	1.2
propene.....	0.6	1.2	2.4
ethane.....	t	t	0.6
ethene.....	—	t	t
ethyne.....	—	t	t
butadiene.....	0.4	0.8	0.5
benzene.....	—	—	—

At a given temperature the beginning of the formation of a slight cloud is observed and at a higher temperature this cloud thickens into visible drops, probably of an oily nature, perhaps indicating the formation of aromatics. Vide Table IX.

Table IX

Experiments recorded in Table No.—	Beginning of formation of cloud at °C.	Formation of drops at °C.
IV.....	950	975
V.....	925	950
VI.....	875	900
VII.....	1,025	1,050
VIII.....	1,000	—

The tables show that with very short contact times for example of less than 0.05 second, a fair yield of propadiene and/or propyne can be obtained without the

substantial formation of decomposition products, especially if temperatures higher than 900° C. are used.

For example, at 1025° C. and a contact time of 0.01 second the amount of C₃-unsaturated hydrocarbons is about 10.8 percent by volume calculated on the initial volume of isobutene; of these C₃-unsaturated hydrocarbons in the final mixture about 50 percent by volume is propadiene, 20% is propyne and 30% is propene. At 950° C. and a contact time of 0.02 second the conversion of isobutene into C₃-unsaturated hydrocarbons is slightly lower, viz. 10.2, and of these C₃-unsaturated hydrocarbons in the final mixture about 50 percent by volume is propadiene, about 18 percent is propyne and about 32% is propene.

Addition of, for example, azomethane does not substantially alter the general picture, but for optimal yields a somewhat lower temperature is found than without azomethane being present.

According to the invention all experiments are essentially carried out at substantially atmospheric pressures.

It has been found that at reduced pressures the process becomes increasingly ineffective, both as to the rate of conversion and as to the undesirable formation of products other than propadiene and/or propyne.

A further advantage of working at a substantially atmospheric pressure according to the invention is that the isolation of the propadiene and/or propyne formed is much easier than in the case of the isobutene being cracked in the presence of a diluent gas, because in the latter type of processes the diluent gas, such as steam, seriously complicates the isolating step.

By "working at substantially atmospheric pressures" in the specification and claims is understood that the partial pressure of the isobutene in the initial feed is substantially 1 atmosphere and that the whole process is carried out at substantially atmospheric pressures. No reduced pressures are used in the process according to the invention, neither is the isobutene diluted with a diluent gas. It stands to reason that a gaseous catalyst such as azomethane is not considered to be a diluent gas.

What is claimed is:

1. A process for the preparation of unsaturated hydrocarbons selected from the group consisting of propadiene and propyne which comprises subjecting substantially undiluted isobutene to a thermal cracking at a temperature above 700° C. at a contact time of less than 0.2 second at substantially atmospheric pressure and recovering said unsaturated hydrocarbons from the resultant cracked mixture.

2. A process for the preparation of unsaturated hydrocarbons selected from the group consisting of propadiene and propyne which comprises the steps of subjecting substantially undiluted isobutene to a thermal cracking at a temperature above 850° C. at a contact time of less than 0.1 second at substantially atmospheric pressure and recovering said unsaturated hydrocarbons from the resultant cracked mixture.

3. The process according to claim 1 in which a gaseous catalyst is used.

4. The process according to claim 3 in which azomethane is the catalyst.

5. The process according to claim 2, wherein the contact time is less than 0.05 second and the temperature is at least about 900° C.

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