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PROCESS FOR CRACKING PROPYLENE AND ISOBUTYLENE IN THE PRESENCE OF HBr

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2 Sheets-Sheet 1

C_3H_6 CRACKING WITH HBR ADDITION

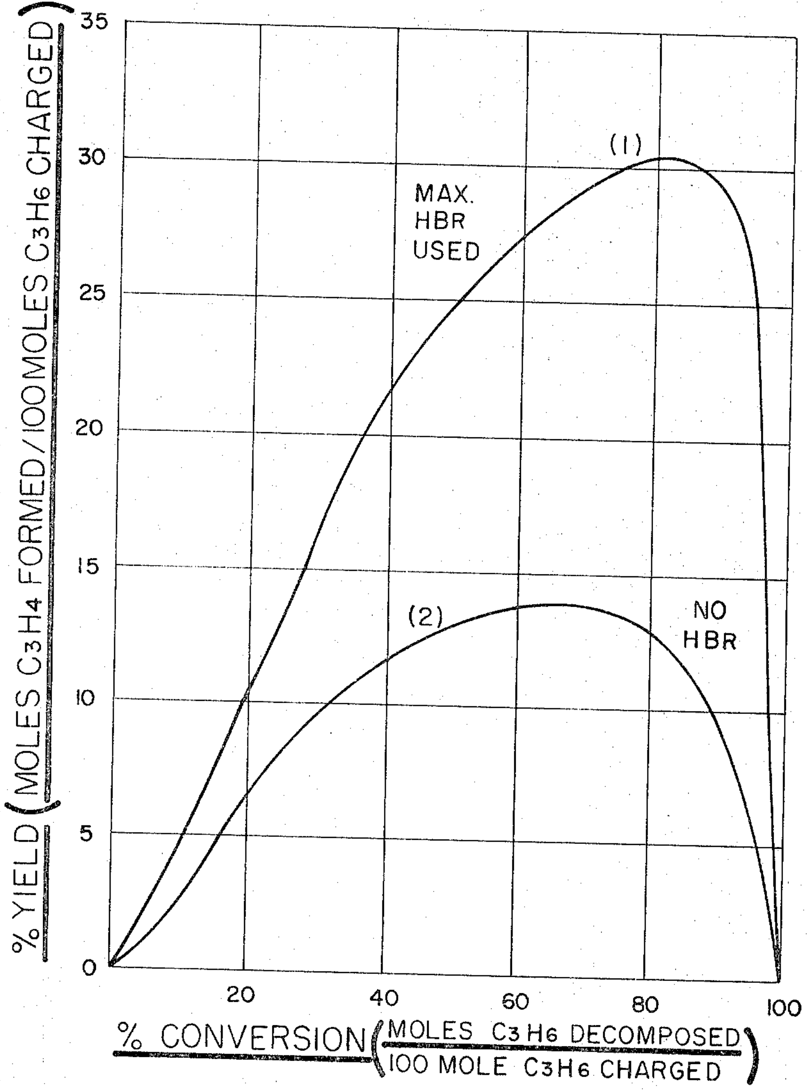

FIGURE 1

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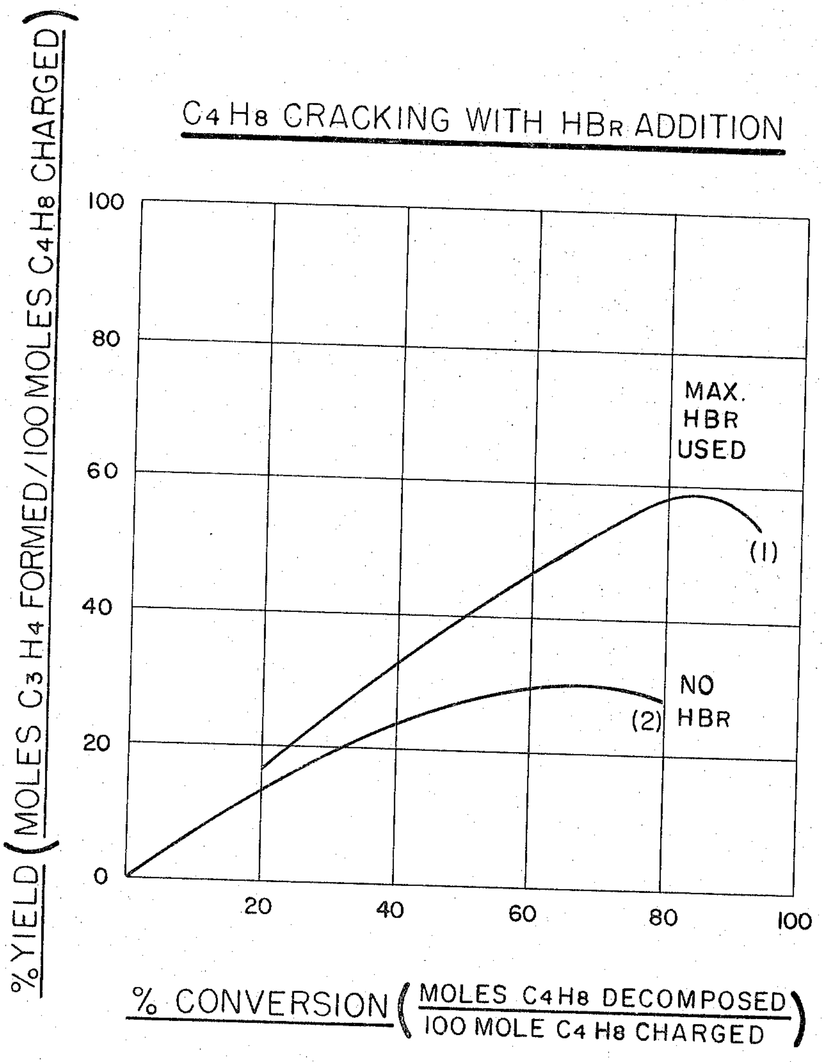

FIGURE 2

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PROCESS FOR CRACKING PROPYLENE AND ISOBUTYLENE IN THE PRESENCE OF HBr

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This invention relates to a novel and improved catalytic thermal process for making mixtures of methyl acetylene and allene from isobutylene and/or propylene. In particular, the invention pertains to a process whereby isobutylene and/or propylene is cracked under special conditions in the presence of a hydrogen bromide or hydrogen bromide itself to give improved yields of the desired methyl acetylene and allene.

It is well known that olefins such as isobutylene and propylene undergo thermal decomposition or cracking when subjected to elevated temperatures in an inert atmosphere for prescribed periods of time. It is also known that the cracking of isobutylene or propylene at ordinary conditions results in relatively small yields or methyl acetylene and allene in the cracked products. In efforts to improve the yields of the desired methyl acetylene and allene, it has been found necessary to conduct the cracking under special conditions of greatly reduced pressure as well as carefully controlled temperature and contact time. This method of operation has proved commercially unattractive mainly because of the inherent problems in obtaining reduced pressures at high temperatures. These difficulties are especially severe in commercial operations. Among these problems are the need for expensive equipment, problems in process control and poor heat transfer characteristics, all of which tend to be intensified when brought to commercial scale operations.

One of the more recently proposed methods of overcoming the difficulties of the prior art processes is described in U.S. Patent No. 2,763,703 issued to the present inventors on September 18, 1956. It is disclosed therein that at temperatures within the range of about 800° C. to 900° C. and at contact times ranging from 0.01 to 10 seconds, a preferred mixture of about 80 to 90 mole percent steam and 20 to 10 mole percent isobutylene, when cracked at atmospheric pressure yields up to 5 mole percent conversion of isobutylene to methyl acetylene and simultaneously an equal amount of allene in a single pass. The present inventors have also shown that as an improvement thereover, at temperatures in the range of 1050° C. to 1150° C. and a contact time of 0.001 to 0.06 second an identical mixture as above, of about 80 to 90 mole percent steam and 10 to 20 mole percent isobutylene, when cracked at atmospheric pressure gave up to 25 mole percent conversion to isobutylene to both methyl acetylene and allene in a single pass. This data indicates that short contact times tend to increase the yield of the desired products. It was first revealed in this patent that good yields of methyl acetylene and allene were obtained by cracking isobutylene though the cracking occurs at essentially one atmosphere total pressure in the presence of an inert diluent. One atmosphere is the most convenient pressure for commercial operation. A carefully controlled contact time was also found to be particularly important in determining the products resulting from either of these two cracking processes. Prolonged contact time of the isobutylene feed in the cracking zone was found to cause breaking of the carbon chain of the isobutylene molecule to give predominantly carbon monoxide and acetylene. Prolonged contact time has also been found to result in decreased yields of methyl acetylene and allene since these products are cleaved by thermal decomposition. At the same time, however, it has been found necessary that the contact time be sufficiently long to allow for the demethanization of the isobutylene molecule for production of the desired methyl acetylene and allene. One way to obtain this required close control on contact time, is to cool rapidly the hot reactor exit gases to a point below which further significant thermal decomposition will occur. This rapid cooling operation has been termed "shock quenching." It has also been disclosed that steam is a particularly advantageous diluent to use when cracking at an overall pressure of one atmosphere or greater. This is true not only because of the fact that steam is an economical diluent and can readily be condensed out of the exit reactor gases, but also because steam suppresses the formation of coke and therefore decreases the loss of methyl acetylene and allene to this worthless product.

There have been numerous efforts to develop commercially attractive processes for the production of methyl acetylene and allene which attempt to avoid the difficulties of the prior art processes and also yield greater amounts of the desired methyl acetylene and allene. U.S. Patent No. 2,925,451 issued to M. J. Hogsed on February 16, 1960, proposed converting isobutylene or propylene to methyl acetylene and allene by passage over a metallic filament of high resistivity, such as platinum or Nichrome, heated to temperatures of at least 900° C. In addition, the Hogsed process teaches use of a reaction pressure of less than 0.01 atmosphere. Improved yields of methyl acetylene and allene, especially allene are disclosed. One major disadvantage of the Hogsed process, however, is its lack of utility as a commercial operation. This is because of the necessity of operating under vacuum with all its inherent disadvantages and also the fact that only small throughputs are possible. The possibility that the hot wire may act as a catalyst also tends to make scaleup to commercial operation difficult.

The basis of the present invention is the discovery that when isobutylene or propylene is cracked in the presence of hydrogen bromide or a hydrogen bromide yielding compound, the presence of the hydrogen bromide acts to direct and improve the cracking in such a way so as to increase the yield of the more valuable methyl acetylene and allene at the expense of the less desirable by-products of the cracking process. It is the object of this invention to provide a catalytic cracking process for making methyl acetylene and allene from isobutylene or from propylene which avoids the diffiiculties of the prior art by operating at essentially atmospheric pressure with short contact times using an inert diluent, preferably steam, and at the same time, by the addition of hydrogen bromide or a hydrogen bromide yielding compound, producing unexpected high yields of the desired methyl acetylene and allene. Thus, the disadvantages of each of the processes of the prior art are avoided. It has been found that, at high conversion levels, the presence of hydrogen bromide or hydrogen bromide yielding compounds in the cracking process nearly doubles the yield of the desired products. It is surprising and unexpected that such results can be obtained since in the prior art some hydrocarbons including propylene have actually been suggested as inert diluents for cracking other substrates in the presence of hydrogen bromide.

Actual experimental data on the results of cracking propylene with and without the presence of hydrogen bromide are presented graphically in the accompanying FIGURE 1 which shows the outstanding improvement in yield obtained by the catalyst addition. From actual operating data obtained, a smooth curve has been drawn through the points in the accompanying plot for the range of conversion. At high conversion levels, the presence of hydrogen bromide in the cracking process more than doubles the yield of desired products.

The term "conversion" in this specification is used to nean the ratio of the moles of propylene cracked to other roducts per mole of propylene charged to the reactor or a single pass. The term “selectivity” is used to mean atio of the moles of C_3H_4 hydrocarbons (methyl acetyene and allene) obtained per mole of propylene consumed to other products for a single pass. The term “yield” as used in the specification means the ratio of the moles of C_3H_4 hydrocarbons formed per mole of propylene feed to the reactor. Used this way, yield is also equal to the product of the conversion multiplied by the selectivity. The accompanying graph of actual experimental data is a plot of yield versus conversion.

It will be noted from the accompanying Figure 1 (curve 2) that yield drops off rapidly for higher conversions when cracking without catalyst addition. For cracking with catalyst addition (curve 1), however, it will be noted that yields steadily increase with conversion and reach a maximum at the very high conversion of about 85–90%, which is a highly desirable result for commercial cracking operations.

A table (Table I) of actual experimental data is included hereinafter in the examples, to describe more fully the improvement obtained by hydrogen bromide yielding compound addition in the cracking of propylene. It will be noted from this table that the selectivity of the desired C_3H_4 hydrocarbons obtained tends to increase with an increasing ratio of hydrogen bromide to propylene in the infeed to the reactor. It will also be noticed that the increased yields of methyl acetylene and allene are achieved at the expense of the less useful byproducts of the cracking, which is most desirable.

Actual experimental data from the cracking of isobutylene with and without the addition of hydrogen bromide are shown graphically in the accompanying FIGURE 2 and shows the outstanding improvement obtained by the catalyst addition. For the actual operating data obtained, a smooth curve has been drawn through the points in the accompanying plot for the range of conversions.

The accompanying FIGURE 2 of the actual experimental data is a plot of yield versus conversion. It will be noted from the accompanying graph (curve 2) that the yield drops off rapidly for higher conversions when cracking without catalyst addition. For cracking with hydrogen bromide (curve 1) addition, however, it will be noticed that yields steadily increase with conversion and reach a maximum at the very high conversion of about 80–85%, which is a highly desirable result for commercial operation. This a very unexpected and unpredictable result using hydrogen bromide or hydrogen bromide producing compounds, i.e., HBr forming at the conditions and with the materials in the cracking zone. It will be noticed from the accompanying table (Table 2) that the selectivity of the desired C_3H_4 hydrocarbons obtained tends to increase with an increasing ratio of hydrogen bromide to isobutylene in the feed to the reactor. It will also be noticed that the increased yields of methyl acetylene and allene are achieved at the expense of the less useful byproducts of the cracking which is, of course, most desirable.

It has been found that improvements in yields of desired product are obtained from about 5 moles of HBr per 100 moles of olefin, and that yields tend to increase steadily up to ratios of over 60 moles of HBr per 100 moles of olefin. In carrying out the process, the reaction zone contact time should be within the range of 0.0005 to 0.06 second, while the mole percentage of steam to olefin feed may be varied between 40 and 95 percent. The preferred contact times are in the range of 0.001 to 0.005 seconds. Reaction pressures for the isobutylene will vary from about 0.05 to 0.30 atmospheres or about 38 to 225 mm. Hg by dilution and total pressure may be kept conveniently at one atmosphere. The molar ratio of hydrogen bromide to isobutylene may be varied from as low as required depending on the aims of the process up to a maximum which is dictated by economics. The lower practical limit of hydrogen bromide to isobutylene was found to be about 5 moles of HBr per 100 moles of olefin feed, a point at which significant improvements in yield over that obtained without HBr addition becomes apparent. The optimum ratio of HBr to feed is governed generally by the economics of the particular process and will be determined by a balance between the cost of hydrogen bromide recovery and recycle and the savings in plant and operating cost obtained by the increased yields of methl acetylene and allene due to hydrogen bromide addition.

The preferred method of operation for propylene is from a mole ratio of superheated steam to propylene and propylene to hydrogen bromide of 10 to 1 and 1 to 1 moles respectively, up to a mole ratio of superheated steam to propylene and propylene to hydrogen bromide of 4 to 1 and 15 to 1 moles respectively. The preferred contact time is from 0.0005 second to 0.01 second. The effective temperature in the cracking zone is above 900° C. and ranges from 800° C. to 1250° C. The maximum yield of methyl acetylene and allene is obtained at conversions of 70 to 90 percent of the feed.

The preferred method of operation for isobutylene is from a mole ratio of superheated steam to isobutylene and isobutylene to hydrogen bromide of 10 to 1 and 1 to 1 moles respectively up to a mole ratio of superheated steam to isobutylene and isobutylene to hydrogen bromide of 4 to 1 and 15 to 1 moles respectively. The effective temperature range in the cracking zone is from 700° C. to 1150° C. At a temperature of about 800° C., the conversion is low (below 10%). At temperatures of about 1000° C., the conversion is high (above 90%) but the selectivity falls off. It appears that using the above defined reaction conditions, the maximum yield of methyl acetylene and allene is obtained at conversions of 80 to 90 percent.

Concerning the method of carrying out this invention, various methods of achieving the required reaction temperatures may be employed and a number of such methods are illustrated below. It is not intended, however, to limit the invention in any way to any particular method for carrying out the process.

(1) A hot gaseous stream of superheated steam is added to the olefin feed stream, or

(2) The olefin feed stream is passed quickly through an electric arc zone, or

(3) A portion of the olefin gas stream is burned and provides hot combustion gases, which heat up the main feed stream to the desired temperature range, or

(4) Powdered particles of an inert material, e.g., alumina are heated at elevated temperatures and injected into the olefin feed stream.

A particularly advantageous method of achieving the high temperatures for cracking with good control is to mix the olefin feed with superheated steam just prior to its entry into the cracking section. The rapid mixing and diffusion of the two gases because of high velocity and high temperature will very rapidly bring the feed to the desired cracking temperature. It is also advantageous to preheat the olefin feed just prior to mixing in order to conserve on the temperature and use of the superheated steam, but it is not a necessity for the invention that this preheating of the olefin feed occur. It is necessary, however, that the superheated steam entering or admixed be at a temperature greater than that in the cracking zone since it will essentially determine the final temperature of the olefin, steam, and hydrogen bromide or hydrogen bromide yielding compounds, admixture entering the reactor. Another advantage of steam dilution is the fact that the cracking of isobutylene or propylene to methyl acetylene and allene is an endothermic reaction and thus heat is absorbed during the cracking resulting in a temperature drop within the reaction zone. The high temperature steam dilution acts as a heat source to keep the cracking zone at a more constant temperature and provide more accurate control of contact time. The high temperature steam necessary for this purpose can vary in temperature from 1000° C. to 2000° C. as required and this temperature may be obtained in a variety of ways, among them being the use of a high temperature pebble heater, the mixing of low temperature steam with the very hot steam product from the burning of hydrogen and oxygen to give the desired high temperature steam or the use of electrical heating. The superheated steam diluent need not be sure, but may also be mixed with gases obtained by the combustion of a fuel. It is more desirable, however, that the steam be essentially pure since this will allow for substantially complete condensation of the diluent from the cracked gases. This will reduce the problem of purifying these cracked gases since they enter the purification system undiluted by the extraneous gases of the dilution steam mixture. Therefore, by using relatively pure dilution steam, the cracked gases reach the purification system at their maximum concentration for the most efficient recovery of the desired methyl acetylene and allene. The additional advantage of using steam dilution to prevent coke formation is also of value.

Careful control of contact time is necessary in order to obtain the required conditions of this process. Contact time is defined as the volume of the reaction zone divided by the volume of feed at the reaction temperature. As previously mentioned, the cracking is an endothermic reaction and there is a varying temperature profile throughout the length of the reactor. Therefore, the proper integrated effective temperature must be used in order to determine the volume of the gaseous feed through the reaction zone. The contact time may be varied by varying the rate of gases going through the reactor. Variation of temperature will also vary contact time by changing the volume of the feed through the reaction zone. Contact time can also vary for a given fixed feed by replacement with reactors of various volumes or using a series of reactors with fixed cross section but with varying lengths. Rapid termination of contact time is best obtained by direct contact with a deluge of water or oil. It is also possible to contact the reaction zone gases with cool gases or powdered, inert material such as alumina, the method of cooling being unimportant so long as the exit reactor gases are cooled very quickly to below at least 500° C. This rapid cooling serves to prevent thermal decomposition of reaction products, prevent polymerization and to control contact time.

The hydrogen bromide additive of this invention may be added in many forms, as a liquid or vapor depending on the compound and the pressure. It is also possible to use an organic or mineral compound containing bromine which under the cracking conditions in the reactor decomposes to yield required amounts of a bromide of the form such that it is recovered as hydrogen bromide. If a mineral compound is used which liberates hydrogen bromide under the conditions in the reactor, it is convenient to dissolve it in water which is subsequently converted to steam and then acts as the inert diluent for cracking.

Representative of organic bromine compounds which may be used in the reaction are ethyl bromide, 2 bromopropane, 1-bromobutane, and the like. Mineral bromine compounds which may be used in the process of the invention are hydrobromic acid and water soluble bromine compounds. Suitable compounds in the scope of the invention must decompose or dissociate under the conditions of the reaction to form hydrogen bromide. An economic method of introducing a hydrogen bromide yielding compound is to use HBr as the reagent. The mixture of HBr and steam after passing through the cracking zone is readily recovered in the quench system. If the exit gases from the cracking reactor are quenched with water, a dilute solution of the HBr originally fed is obtained. If the exit gases are quenched with another material such as an oil, the HBr dissolves in the condensed steam. Recovery of the HBr for reuse in the cracking zone may be accomplished by distillation, absorption or any other well known means.

This invention may be carried out with pure isobutylene or pure propylene or with a commercial fraction containing these compounds such as is obtained by distillation or extraction in a petroleum operation or the like.

The invention will be more fully understood by reference to the following illustrative examples of the preferred methods of operation, however, these examples are for illustration only and are intended in no way to limit the invention specifically thereto.

Example 1

A propylene feed stream is metered and intimately mixed with superheated steam and HBr just before introduction into a 9″ long schedule 80 stainless steel reactor. The mole ratio of steam to propylene is kept at about 6.7 to 1. The temperature in the center of the reactor is about 1015° C. and the contact time is 0.00207 second. The resulting propylene conversion is 55.6% and selectivity of allene and methyl acetylene obtained is 23.6% as determined by exit gas analysis. While these flows are held constant, HBr is added at a molar ratio of 0.078 mole of HBr per mole of propylene. The temperature is determined to be 1028° C. The resulting conversion is 56.3% and the selectivity of methyl acetylene and allene is 34.3% as determined by exit gas analysis. The HBr mole ratio is then increased to 0.117 mole of HBr per mole of propylene. The temperature is 1030° C. as read by a thermocouple. Conversion is 56.9% and selectivity is 39.1% as determined by exit gas analysis. The HBr is then increased to 0.526 mole of HBr per mole of propylene, and temperature is determined to be 1020° C. The conversion is 52.9% and selectivity is 50.4% as determined by exit gas analysis. This series of runs clearly discloses the great improvement obtained by HBr addition into the cracking zone.

Analytical results of the 0.526 HBr to propylene run, after making allowances for excess hydrogen from the burner gas and other sources is given below:

Component:	Mole percent
H_2	29.50
O_2	0.77
N_2	0.92
CH_4	14.71
C_2H_4	6.15
CO_2	0.47
C_3H_8	0.03
C_3H_6	25.58
C_2H_2	7.14
Allene	5.41
Methyl acetylene	9.10
C_4H_6	0.23

Example 2

A propylene feed stream is metered before being introduced into an experimental inconel cracking tube which is one-half inch schedule 80 and 11 inches long. Measured quantities of superheated steam and hydrogen bromide are then intimately mixed with propylene just prior to the reactor tube entrance. The superheated steam which has been previously heated in a zone where hydrogen-oxygen combustion is taking place, is passed into the reactor. The mole ratio of steam to propylene is 6.7 to 1. The total reactor pressure is kept at about one atmosphere during the reaction and a thermocouple in the middle of the cracking tube registers a temperature of 1080° C. The contact time of reaction as determined by the effective temperature is about 0.0036 second and the resulting conversion is 56.8%. A water quench is used immediately following the reaction zone and after steam condensation and water removal, the effluent gas is analyzed. From this data selectivity is determined to e 31.9% for methyl acetylene and allene. While these ows are held constant, HBr is introduced at a molar atio of 0.078 mole of HBr per mole of propylene. The mperature is determined to be 1100° C. The resulting onversion is 52.7% and the selectivity of methyl acetylne and allene are determined to be 32.3%. The HBr nole ratio is then increased to 0.117 mole of HBr per nole of propylene. The temperature is 1085° C. and the onversion is 51.6%. The selectivity as determined by xit gas analysis is 42.8%. Again the HBr mole ratio s increased to 0.526 mole HBr per mole of propylene, and he conversion is 52.0%. The selectivity as determined by xit gas analysis again increased to 47.0%.

Example 3

The data in the following Table I was obtained using lifferent size reactors as so indicated in the table. The effect of intermediate quantities of hydrogen bromide are shown. Conditions are used and results obtained as shown.

TABLE I.—THERMAL CRACKING OF PROPYLENE

Experiment Number	Moles $\frac{HBr}{C_3H_6}\times 100$	Percent Conversion	Percent Selectivity			Moles Steam $\frac{}{C_3H_6}$	Temperature, ° C.	$\times 10^{-3}$ Contact Time, Seconds	Percent Yield $\frac{C_3H_4}{C_3H_6}$
			C_3H_4	C_2H_4	C_2H_2				
1	0	55.6	23.6	42.2	29.4	6.7	1,015	2.07	13.11
2	7.8	56.3	34.3	34.5	27.1	6.7	1,028	2.03	19.34
3	11.7	56.9	39.1	29.3	25.9	6.7	1,030	2.01	22.26
4	52.6	52.9	50.4	21.4	24.8	6.7	1,020	1.92	26.66
5	0	96.4	6.3	20.7	55.1	6.7	1,190	1.82	6.07
6	7.8	97.7	8.0	15.6	60.3	6.7	1,200	1.79	7.79
7	11.7	98.1	9.3	13.3	66.3	6.7	1,200	1.78	9.12
8	52.6	98.7	11.7	9.0	69.2	6.7	1,180	1.71	11.55
9	0	84.5	19.1	33.1	44.0	6.7	1,075	2.01	16.14
10	7.8	85.4	20.8	26.3	44.7	6.7	1,085	1.98	17.76
11	11.7	86.5	23.8	23.4	45.6	6.7	1,085	1.96	20.59
12	52.6	84.6	36.5	17.3	43.0	6.7	1,075	1.87	30.88
13	0	7.1	23.2	30.5	4.3	6.7	830	3.53	1.65
14	7.8	5.5	23.7	24.9	1.2	6.7	835	3.47	1.30
15	11.7	6.6	30.3	31.5	3.4	6.7	830	3.47	2.00
16	52.6	5.6	37.9	25.6	3.8	6.7	825	3.31	2.12
17	0	35.0	28.3	43.7	20.3	6.7	965	3.22	9.91
18	7.8	37.9	38.7	37.1	18.5	6.7	980	3.15	14.67
19	11.7	35.1	44.6	32.1	18.5	6.7	975	3.15	15.65
20	52.6	31.5	54.3	22.8	17.3	6.7	955	3.03	17.10
21	0	14.9	28.8	35.8	8.0	6.7	860	3.63	5.78
22	7.8	15.4	39.2	40.2	9.2	6.7	885	3.53	6.04
23	11.7	15.1	42.2	37.3	9.5	6.7	880	3.27	6.39
24	52.6	11.9	52.3	29.4	9.5	6.7	880	3.09	6.22

The above runs were made in a 9″ long stainless tube ½″ Schedule 80

Experiment Number	Moles $\frac{HBr}{C_3H_6}\times 100$	Percent Conversion	C_3H_4	C_2H_4	C_2H_2	Moles Steam $\frac{}{C_3H_6}$	Temperature, ° C.	$\times 10^{-3}$ Contact Time, Seconds	Percent Yield $\frac{C_3H_4}{C_3H_6}$
25	0	56.8	31.9	32.2	30.3	6.7	1,080	3.59	18.12
26	7.8	52.7	32.3	34.6	29.2	6.7	1,100	3.50	17.02
27	11.7	51.6	42.8	32.1	29.4	6.7	1,085	3.52	22.08
28	52.6	52.0	47.0	21.7	28.6	6.7	1,065	3.39	24.44

The above runs were made in an 11″ long Inconel tube ½″ Schedule 80

Example 4

An isobutylene feed stream is metered and then preheated before being introduced into an experimental stainless steel cracking tube which is one-half inch Schedule 80 and is 9 inches long. Measured quantities of superheated steam and hydrogen bromide are then intimately mixed with the isobutylene just prior to the reactor tube entrance. The superheated steam which has been previously heated in a zone where hydrogen-oxygen combustion is taking place, is passed into the reactor. The mole ratio of steam to isobutylene and isobutylene to hydrogen bromide are 9 to 1, and 1.57 to 1 respectively. The total reactor pressure is kept at about one atmosphere during the reaction and a thremocouple in the middle of the cracking tube registers a temperature of 995° C. and the exit temperature from the pyrolysis tube is 902° C. The isobutylene is added after being preheated to a temperature of 200° C. The contact time of reaction as determined by the effective temperature is about 0.0015 second and the resulting isobutylene conversion is 74.6 percent. A water quench is used immediately following the reaction zone and after steam condensation and water removal, the effluent gas is analyzed. From this data, selectivity was determined to be 73.4 percent. Analysis of the reaction products was obtained after making allowances for the excess hydrogen from the burner gas and for other gases which were obtained from sources other than the cracking reaction and the analytical results are given below.

Component:	Mole percent
Hydrogen	7.17
Oxygen	2.47
Nitrogen	0.35
Methane	40.88
Carbon monoxide	2.18
Ethane	0.10
Ethylene	1.73
Carbon dioxide	0.57
Propylene	1.67
Acetylene	3.86
n-Butane	0.03
Allene	11.59
Isobutylene	12.09
Methyl acetylene	14.40
Butadiene	0.90
Total	99.99

Example 5

An isobutylene feed stream is metered and then preheated before being introduced into a stainless steel tube of the same dimensions as previously given in Example 4 above. Measured quantities of superheated steam and isobutylene are intimately mixed just prior to the reactor tube entrance. The mole ratio of steam to isobutylene is 10 to 1. The temperature in the reactor tube is about 1020° C. The contact time is determined to about .0013 second. The resulting isobutylene conversion is 80.2 percent and selectivity for methyl acetylene and allene is 38.6 percent as determined by analysis of the exit gas. While these flows are kept essentially constant, HBr is added at a molar ratio of 11.8 moles of isobutylene feed to 1 mole of HBr. The temperature is determined to be about 1020° C. The resulting conversion is 85.8 percent and selectivity rose to 46.4 percent as determined by analysis of the exit reactor gas. The ratio of HBr to isobutylene is then increased to 7.55 moles of isobutylene to 1 mole of HBr. Analysis of the exit gas revealed that a conversion of 82.8 percent and selectivity of 51.4 percent is obtained. And again, the ratio of HBr to isobutylene is increased to 0.9 moles of isobutylene per mole of HBr. Analysis of the exit gas revealed that a conversion of 94.1 percent and a selectivity of methyl acetylene and allene of 55.5 percent is obtained. This series of runs very clearly points up the improvement obtained by HBr addition into the cracking zone.

Example 6

An isobutylene feed stream is metered and then preheated before being introduced into an 11 inch, one-half inch Schedule 80 Inconel tube. Measured quantities of superheated steam and isobutylene feed are intimately mixed just prior to the reactor tube entrance. The mole ratio of steam to isobutylene is 10 to 1. The temperature in the reactor tube is about 975° C. The contact time is determined to be about .0033 second. The resulting isobutylene conversion is 22.4 percent and selectivity of methyl acetylene and allene is 66.3 percent as determined by analysis of the exit gases. While these flows are kept essentially constant, HBr is added at a molar ratio of 11.8 moles of isobutylene feed to 1 mole of HBr. The temperature is determined to be about 960° C. The resulting conversion is 27.8 percent and the selectivity increases to 72.2 percent as determined by analysis of the exit gases. The ratio of HBr to isobutylene is increased to 7.55 moles of isobutylene to 1 mole of HBr. Analysis of the exit gas reveals that a conversion of 31.9 percent and a selectivity of 73.30 percent is obtained. The ratio of HBr to isobutylene is increased to 0.9 moles of isobutylene per mole of HBr. Analysis of the exit gas revealed that a conversion of 35.6 percent and selectivity of 80.5 percent is obtained.

Example 7

The data in the following Table II was obtained using different size reactors as indicated in the table. The effect of intermediate quantities of hydroben bromide are shown. Conditions were used and results obtained as shown.

TABLE II.—THERMAL CRACKING OF ISOBUTYLENE

Experiment Number	Mole Ratio $\frac{HBr}{Iso}\times100$	Percent Conversion	Percent Selectivity			Mole Ratio $\frac{Steam}{Iso}$	Contact Time, Secs.	Reactor Temp., ° C.
			C_3H_4	C_2H_4	C_2H_2			
Using a 9" long one-half inch Schedule 80 stainless tube								
101	0	22.1	66.4	6.1	7.3	10	0.0017	935
102	47.0	36.5	79.5	3.7	4.5	10	0.0016	930
103	0	55.7	51.8	11.8	18.8	10	0.0016	985
104	64.0	74.5	73.4	4.9	10.9	10	0.0015	995
105	46.7	76.0	69.1	5.2	12.4	10	0.0016	1,000
106	67.9	76.0	71.2	5.8	12.6	10	0.0015	990
107	0	80.2	38.6	16.0	36.7	10	0.0013	1,020
108	7.8	85.8	46.4	11.4	32.4	10	0.0013	1,020
109	11.7	82.8	51.4	12.7	31.4	10	0.0013	1,015
110	52.6	94.1	55.5	6.3	24.9	10	0.0013	1,020
For an 11" Inconel reactor of the same diameter as previously given								
111	0	22.4	66.3	8.1	10.9	10	0.0033	975
112	7.7	27.8	72.2	5.3	7.5	10	0.0033	945
113	11.0	31.9	73.3	4.9	6.4	10	0.0033	950
114	52.6	35.6	80.5	3.5	4.9	10	0.0033	955

What is claimed is:

1. A process for preparing allene and methyl acetylene from propylene which comprises subjecting a mixture of propylene and hydrogen bromide or a bromide containing material capable of yielding hydrogen bromide at the reaction conditions, the mole ratio of propylene to hydrogen bromide being from 1 to 1 to 15 to 1, to a temperature of above 900° C. for from about 0.0005 to 0.01 second and under conditions such that about 70 to 90 percent of the propylene is converted, and separating allene and methyl acetylene from the resulting product.

2. A process for preparing allene and methyl acetylene from isobutylene which comprises subjecting a mixture of isobutylene and hydrogen bromide or a bromine containing material capable of yielding hydrogen bromide at the reaction conditions, the mole ratio of isobutylene to hydrogen bromide being from 1 to 1 to 15 to 1, to a temperature of above 700° C. for from about 0.0005 to 0.06 second, and under conditions such that about 80 to 90 percent of the isobutylene is converted and separating allene and methyl acetylene from the resulting product.

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