United States Patent Office 3,188,356 Patented June 8, 1965

3,188,356

METHOD FOR PRODUCING VINYLIDENE FLUORIDE

Murray Hauptschein, Glenside, and Arnold H. Fainberg, Elkins Park, Pa., assignors to Pennsalt Chemicals Corporation, Philadelphia, Pa., a corporation of Pennsylvania

No Drawing. Filed Nov. 8, 1961, Ser. No. 150,898
8 Claims. (Cl. 260—653.5)

This invention relates to an improved method for the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane to produce vinylidene fluoride.

It is known that 1,1,1-trifluoroethane, CH_3CF_3, can be dehydrofluorinated by heating at elevated temperatures. This reaction is described in U.S. Patent 2,480,560 which recommends pyrolysis temperatures of from 600 to 1000° C. Examples of the pyrolysis of CH_3CF_3 (Examples I and II) are given at temperatures ranging from 750° C. to 910° C. According to this patent, a mixture of products is obtained including substantial amounts of high boiling materials.

In accordance with the present invention, it has now been unexpectedly found that there are many marked advantages to be obtained by carrying out the pyrolysis at temperatures well above those previously recommended. It has been found that by carrying out the pyrolysis of CH_3CF_3 at temperatures of from 1050 to 1500° C. and preferably from 1100 to 1300° C., it is not only possible to obtain high conversions to vinylidene fluoride at very high throughputs, but that along with these advantages there is also obtained a marked and completely unexpected improvement in the selectivity of the pyrolysis reaction with respect to vinylidene fluoride. At the lower temperatures previously recommended, at the relatively low space velocities required to obtain an acceptable conversion, there is obtained, in addition to vinylidene fluoride, both high boiling and low boiling side products. The high boiling materials, i.e. boiling well above the boiling point of $CH_2=CF_2$ may typically represent a yield loss of from 5% to 25%. The low boiling side products, i.e. boiling close to $CH_2=CF_2$, consist of materials such as fluoroform, acetylene, vinyl fluoride, and tetrafluoroethylene, and may typically represent a yield loss of the order of 5%. These low boiling materials are undesirable not only in that they represent a substantial yield loss, but because they are difficult to separate from vinylidene fluoride.

In contrast to the relatively poor selectively of the pyrolysis reaction under these previously described conditions, under the pyrolysis conditions of the invention, involving higher temperatures and very short contact times, it is possible to obtain almost quantitative yields of vinylidene fluoride, with often less than two percent yield losses due to high and low boiling side products. Of particular note is the fact that the production of low boiling materials, difficult to separate from $CH_2=CF_2$, may be readily reduced to levels of well under 1%. This greatly simplifies the problem of purifying the vinylidene fluoride product, since it is feasible to separate such small amounts of low boiling side products by adsorption techniques, molecular sieves or the like, whereas it would be necessary to employ expensive distillation techniques to separate the much larger quantities of these low boilers produced in accordance with prior processes.

This very marked in the selectivity of the pyrolysis reaction at higher temperatures is completely unexpected. While it is recognized that the use of higher temperatures in pyrolysis reactions favor higher conversions per pass and higher throughputs, it is also recognized that as the reaction temperature increases, the probability of side reactions giving unwanted byproducts also increases, and indeed as the temperature increases beyond certain levels, complete degradation of the starting material occurs. It would be expected accordingly that at higher temperatures, the selectivity of the pyrolysis reaction would fall off, and that at the higher energy levels prevailing side reactions would occur at an increasing rate. This would tend to be true particularly for degradation reactions, such as those producing one carbon compounds, e.g. CHF_3 and CH_2F_2, resuluting from carbon bond scission. Contrary to these expectations however, there is instead obtained, in accordance with the invention, a many fold decrease in the amount of both high boiling and low boiling side products, as will be illustrated by the detailed examples which follow.

In combination with the high temperature specified, it is critical to use very short contact times, namely contact times less than about 0.3 second and preferably less than about 0.1 second. At contact times of the usual order of magnitude employed in pyrolysis reactions of this type, typically of the order of 3 to 8 seconds, the process of the invention would be inoperative due to the thermal degradation of the reactants and reaction products. In general, the higher the temperature, the shorter the contact time which will be used. The lower limit of contact time is set only by practical considerations such as pressure drop through the reactor and the desired rate of conversion. Generally, it will not be less than about 0.0001 second. Preferred contact time will generally range from about 0.001 to 0.1 second.

As used herein, contact time is defined as follows:

$$\text{Contact time (seconds)} = \frac{\text{heated reactor volume}}{\text{volume of gas per second (calculated at reaction temperature and pressure) fed to reactor}}$$

The reaction temperature is taken as the observed temperature of the reactor wall (measured e.g. by a thermocouple in contact with the outside wall) near the center of the heated zone where the rate of heat loss to the surroundings is at a minimum. In determining heated reactor volume portions of the heated zone substantially below reaction temperature are ignored. Thus for example, where the reactor takes the form of a tube surrounded by a furnace, the tube wall temperature may tend to fall off rapidly at either end of the furnace due to rapid transfer of heat to the cooler surroundings and/or cooling by incoming reactants, and accordingly those substantially cooler portions of the tube adjacent the ends of the furnace are ignored in determining the heated reactor volume.

It is to be understood that the optimum contact time at any given reaction temperature will be influenced to some extent by factors such as reactor design, the extent to which the reactant is preheated, and the character of the gas flow through the reactor, i.e. whether turbulent or laminar, since these factors influence the approach of average gas temperature to reactor wall temperature. Other conditions being equal, preheating the reactants, and smaller reactor cross sections favor closer approach of gas to reactor wall temperature and accordingly favor shorter contact times. Similarly, conditions providing turbulent as distinguished from laminar flow also favor a closer approach of gas to reactor wall temperature and correspondingly shorter contact times.

The short contact times indicated above correspond to very high space velocities ranging from 2000 to 200,000 per hour and higher. [Space velocity is defined as volumes of reactant (measured at standard temperature and pressure (STP), i.e. 0° C. and 760 mm. Hg) per volume of heated reactor per hour.] This is in sharp contrast to the much lower space velocities previously employed in

this reaction, typically of the order of 100 to 500 per hour. Preferred space velocities in accordance with the invention will generally range from 5,000 to 100,000 per hour. Such high throughputs have the important advantage of greatly reducing reactor volume.

As previously stated, the reaction temperature in accordance with the invention is maintained within the limits of about 1050° C. to 1500° C. and preferably from about 1100° C. to 1300° C. At temperatures below about 1050° C. the desired combination of high space velocities, high conversions per pass and very high yields is not obtained, while at temperature above about 1500° C. it becomes difficult, as a practical matter, to maintain the extremely low contact times necessary to avoid thermal degradation of the reactants. In the preferred range of 1100° to 1300° C., the optimum combination of high space velocities, high conversions and close to quantitative yields, together with optimum ease of operation, will generally be obtained.

The pyrolysis reaction is conveniently carried out by continuously passing a stream of the starting material through an elongated tube preferably having a high ratio of wall area to cross sectional area so that heat may be rapidly and continuously transferred from the heated reactor walls to the gaseous reactants. The tube may have any desired cross sectional shape, such as circular, elliptical, oval or the like and should be constructed of materials resistant to attack by the reactants or reaction products at the operating temperatures. Preferred materials of this type include for example, platinum, or platinum lined tubes, platinum alloys such as platinum-rhodium. Other materials such as nickel or nickel alloys also may be used.

Reaction pressure is not critical and may be atmospheric, sub-atmospheric, or super-atmospheric. While atmospheric pressure operation will generally be found most convenient, sub-atmospheric pressures, ranging as low as about 25 mm. Hg as a practical limit, may be found useful in some cases. Super-atmospheric pressures may range, e.g. up to about 10 atmospheres. Preferred operating pressures will generally range from 100 mm. Hg to atmospheric pressure.

The following examples are intended to illustrate specific embodiments of the invention.

EXAMPLE 1

1,1,1-trifluoroethane is passed through a platinum lined Inconel tube having a 6 mm. inside diameter. A middle 6" section of the tube is maintained at a tube wall temperature of 1200° C. by means of an electric furnace concentric with the tube. Temperature is measured with a platinum-10% platinum-rhodium thermocouple in contact with the outside surface of the reactor tube in the center of the furnace. The exit gases are passed through a tube packed with sodium fluoride heated to 100° C. to remove hydrogen fluoride and are then collected in a liquid nitrogen cooled trap. The reactor and the product handling system including the cooled receivers and hydrogen fluoride scrubber are maintained at a reduced pressure of about 130 mm. Hg.

The flow of CH_3CF_3 is adjusted to a space velocity of 9700 volumes (at STP) per hour per volume of heated reactor space, corresponding to a contact time of 0.01 second.

Low temperature fractional distillation of the organic product readily separates a vinylidene fluoride fraction (B.P. —85° C. at atmospheric pressure); a fraction of unreacted CH_3CF_3 (B.P. —47.5° C. at atmospheric pressure); and a small residue consisting of a complex mixture of higher boiling products (boiling approximately from —40° to over 100° C.). The vinylidene fluoride fraction is shown to be 99.5% pure by gas chromatography. The small amount of impurities in the $CH_2{=}CF_2$ are shown by gas-liquid chromatographic separation and infrared spectral analysis to consist principally of fluoroform, acetylene, vinyl fluoride, and tetrafluoroethylene.

There is obtained a total conversion of CH_3CF_3 to product of 75.4%; a conversion to $CH_2{=}CF_2$ of 74%; a yield of $CH_2{=}CF_2$ of 98.1% with only a 1.4% yield of high boiling side products, and a yield of low boiling side products of only 0.5%.

EXAMPLE 2

In order to demonstrate the marked advantages of the present invention, CH_3CF_3 is pyrolyzed in the manner described in U.S. Patent 2,480,560. The conditions used are substantially those shown in Example II of that patent. CH_3CF_3 is passed at atmospheric pressure through a platinum lined nickel tube and having an 18 mm. inside diameter, the middle section of which is heated to 820° C. The rate of flow of CH_3CF_3 is adjusted to 24 grams per hour. To afford a basis for comparison with Example 1 above, the heated reactor volume is chosen to provide the same total conversion to product as in Example 1 viz. 76%. This results in a heated reactor volume of 38.8 milliliters, giving a CH_3CF_3 space velocity of 200 volumes of CH_3CF_3 (at STP) per volume of reactor per hour, corresponding to a contact time of 4.4 seconds.

The exit gases are treated and collected as described in Example 1. By low temperature fractional distillation of the product there is separated a vinylidene fluoride fraction, a CH_3CF_3 fraction and a substantial amount of high boiling product (B.P. —40° to over 100° C.). The vinylidene fluoride fraction is only 95% pure, being contaminated with 5% of low boiling materials including $CHF{=}CH_2$, $HC{\equiv}CH$, CHF_3 and CH_2F_2. There is obtained a total conversion of CH_3CF_3 to product of 76%, a conversion to $CH_2{=}CF_2$ of 66%; a yield of $CH_2{=}CF_2$ of only 86.5%; a yield of high boiling side products of 8.5% and a yield of low boiling side products of 5%.

Table I below, comparing the results obtained in Examples 1 and 2 at equal rates of conversion when operating respectively at 1200° C. and 820° C. shows the striking advantages of the high temperature operation:

Table I

	Example 1	Example 2
Temperature, ° C.	1,200	820
Contact time (seconds)	0.01	4.4
Space velocity/hour	9,700	200
Total conversion to products, mole percent	75.4	76
Conversion to $CH_2{=}CF_2$, mole percent	74	66
Percent yield of $CH_2{=}CF_2$	98.1	86.5
Percent yield of high boiling side products	1.4	8.5
Percent yield of low boiling side products	0.5	5

As can be seen from Table I by operation in accordance with the invention, there is obtained a fifty fold increase in the throughput rate (space velocity) at the same total conversion to product. The yield of vinylidene fluoride is increased from less than 87% to over 98%. The low boiling, difficulty separable impurities in the vinylidene fluoride fraction are lowered ten fold, namely from 5% to 0.5%. This greatly simplifies the subsequent purification to obtain substantially pure $CH_2{=}CF_2$.

EXAMPLES 3 to 7

In these examples, CH_3CF_3 is passed through a platinum tube having an inside diameter of 2.4 mm,. heated over about 9" of length (reactor volume 1.05 milliliters) to the temperatures shown in Table II below. As in Example 1, the exit gases are passed through a tube packed with sodium fluoride heated to 100° C. to remove hydrogen fluoride and are then collected in a liquid nitrogen cooled trap. The reactor and the product handling system are maintained at a reduced pressure as shown

in Table II. The results obtained in Examples 3 to 7 at various temperatures, contact times and corresponding space velocities are shown in Table II.

Table II

Example	Temp., ° C.	Input pressure, mm. Hg	Contact time (seconds)	Space velocity per hour	Percent conversion to $CH_2=CF_2$	Percent yield of $CH_2=CF_2$
3	910	115	0.02	6,000	6	99
4	910	140	0.01	13,000	1	99
5	1,100	130	0.02	6,000	77	99
6	1,220	170	0.009	16,000	82	98
7	1,200	225	0.006	30,000	56	99

Table II further illustrates the combination of high conversions, very high throughputs and almost quantitative yields obtained in accordance with the invention. The results of Examples 5, 6 and 7 at temperatures of 1100 to 1220° C. contrast sharply with results obtained in Examples 3 and 4 at 910° C. where at similar space velocities, insignificant conversions were obtained.

EXAMPLES 8–10

Using the same equipment as described in connection with Examples 3 to 7, CH_3CF_3 was pyrolyzed at 900° C. and 1250° C. respectively at atmospheric pressure. The results are shown in Table III below:

Table III

Ex.	Temp., ° C.	Contact time, seconds	Space velocity per hour	Percent conversion to $CH_2=CF_2$	Percent yield of $CH_2=CF_2$
8	900	0.06	15,000	2	99
9	1,000	0.05	15,000	16	99
10	1,250	0.03	20,000	82	98

Examples 8–10 again illustrate the outstanding advantages of very high throughputs, high conversions accompanied by almost quantitative yields obtained by operation in accordance with the invention. Examples 8 and 9 carried out at 900° C. and 1000° C. show the insignificant conversions obtained under similar operating conditions.

We claim:

1. A method for producing vinylidene fluoride by the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane which comprises passing a stream of said fluoroethane through a reactor heated to a temperature of 1050 to 1500° C. at a contact time of less than about 0.3 second.

2. A method in accordance with claim 1 in which said reactor is heated to a temperature of about 1100° C. to about 1300° C.

3. A method for producing vinylidene fluoride by the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane which comprises passing a stream of said fluoroethane through a reactor heated to a temperature of 1050° to 1500° C. at a contact time of less than about 0.1 second.

4. A method in accordance with claim 3 in which said reactor is heated to a temperature of 1100° C. to 1300° C.

5. A method for producing vinylidene fluoride by the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane which comprises passing a stream of said fluoroethane through a tube heated to a temperature of 1050° to 1500° C. at a contact time of about 0.001 to 0.1 second.

6. A method for producing vinylidene fluoride by the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane which comprises passing a stream of said fluoroethane through a tube heated to a temperature of 1100° to 1300° C. at a contact time in the range of from about 0.001 to 0.1 second.

7. A method in accordance with claim 6 in which said pyrolysis is carried out at a pressure of from about 100 mm. Hg to about 1 atmosphere.

8. A method for producing vinylidene fluoride by the pyrolytic dehydrofluorination of 1,1,1-trifluoroethane which comprises passing a stream of said fluoroethane through a tube heated to a temperature of 1050° C. to 1500° C. at a contact time of less than about 0.3 second, at least the lining of said tube being composed primarily of platinum.

References Cited by the Examiner

UNITED STATES PATENTS

2,480,560 8/49 Downing et al. ------ 260—653.5

LEON ZITVER, *Primary Examiner.*

ALPHONSO D. SULLIVAN, *Examiner.*