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Short communication

Thermal chlorofluorination of propyne and propadiene

Randolph K. Belter *

Department of Chemistry and Physics, Southeastern Louisiana University, Hammond, LA 70402, United States

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Abstract

Propyne and propadiene have been found to readily undergo vapor phase catalyzed chlorofluorination. At temperatures to 285 °C, the reaction forms mixtures of $C_3F_4Cl_4$ isomers that differ in composition from mixtures obtained from either propane or propene.

Keywords: Chlorofluorination; Propyne; 1,2-Propadiene; Tetrachlorotetrafluoropropane

1. Introduction

For decades chlorofluorocarbons (CFCs) and bromofluorocarbons have been useful chemicals for refrigeration, solvent, plastic foam manufacture and firefighting applications. The discovery of the harmful nature of these chemicals towards the earth's protective ozone layer has led to the outlawing of the manufacture and use of most of these chemicals. Industry has been forced to find suitable replacements and has done so in many instances with hydrofluorocarbons (HFCs). In firefighting applications Halon-13B1 (CF_3Br) was replaced by HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane). HFC-227ea, like all the chlorine- and bromine-free hydrofluorocarbons, has zero ozone depleting potential.

The firefighting agent HFC-227ea is prepared industrially by the simple addition of HF to hexafluoropropylene (HFP). Hexafluoropropylene is manufactured as a by-product or intentional co-product of tetrafluoroethylene manufacture and is useful as a monomer itself. In order to improve the availability of HFP and/or HFC-227ea, several processes [1–4] have been developed that are independent of TFE manufacture. E.I. Du Pont de Nemours has patented a process for producing hexafluoropropylene by first producing 2-chloro-1,1,1,2,3,3,3-heptafluoropropane, **1**, then hydrodehalogenating it to produce HFP [1] (see Scheme 1). The production of the 2-chloro-1,1,1,2,3,3,3-heptafluoropropane, **1**, is brought about by high temperature, vapor phase chlorofluorination of propane or propene over chromia catalyst.

High temperature chlorofluorination of propane and propene is also described in the US patent application of Great Lakes Chemical Corp. [4]. This process chlorofluorinates either 3-carbon feedstock to produce 2,2-dichloro-hexafluoropropane, **2**. Hexafluoro-substituted **2** is then subjected to more strenuous fluorination conditions to force one more fluorine substitution to occur, producing 2-chloro-1,1,1,2,3,3,3-heptafluoropropane, **1**. A third and final step of vapor phase hydro-dehalogenation replaces the remaining chlorine substituent with hydrogen to produce the ultimate desired product 1,1,1,2,3,3,3-heptafluoropropane, **3**, rather than HFP (see Scheme 2).

In the above mentioned processes, propane or propene are chlorofluorinated with HF and chlorine to produce, at a minimum, hexafluorinated material. In such a reaction, 14 mol of hydrogen chloride (HCl) are generated for every mole of propane converted to **2**. Eight moles of HCl are produced in chlorine-for-hydrogen exchange and 6 mol are produced in fluorine-for-chlorine exchange. Propene fares better as the addition reaction of Cl_2 or HF across the double bond eliminates the generation of 2 mol of HCl.

Excessive HCl generation is problematic to the operation of any hydrofluorocarbon manufacturing facility as it makes for more difficult separation of products and recyclable HF and chlorine from the HCl stream. Further, excessive HCl production by the industry as a whole has made it more and more difficult to dispose of HCl as a product on the open market. Just as the use of propene decreases the amount of HCl produced in chlorofluorination by two equivalents, it is a

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* Tel.: +1 985 549 3529; fax: +1 985 549 5126.
E-mail address: rbelter@selu.edu.

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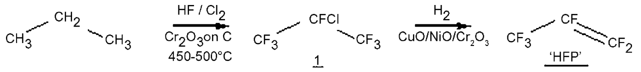
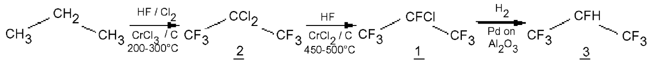


Scheme 1.



Scheme 2.

stoicheometric fact that if propyne could be successfully used as a feedstock for chlorofluorination, it would be possible to produce **1** or **2** with four less equivalents of by-product HCl than is produced with propane. For **2**, that would be a reduction in HCl of 29%. In terms of operation and disposal costs, such a reduction is significant.

The initial goal of this project was to determine whether propyne could, in fact, serve as a viable feedstock for high temperature vapor phase chlorofluorination. Additionally, it became a goal of this project to analyze the isomeric composition of the chlorofluorination products of propane, propene and propyne and to look for variations in those compositions.

2. Results and discussion

2.1. Reaction conditions

Initially, control experiments were run on propane and propene in order to determine acceptable operating parameters for a reactor. Reactions were performed in a single 1 in. (2.5 cm) diameter tubular reactor, 24 in. (61 cm) long, with two electrically heated temperature zones of equal length. As described in the literature [4], it is advisable to perform chlorofluorination reactions of hydrocarbons in two stages. A first stage reaction is performed at a lower temperature of between 225 and 285 °C in order to mitigate the exotherm of initial chlorination. A second stage reaction is then performed at a higher temperature of approximately 450–500 °C to encourage more complete fluorine for chlorine exchange. For the purposes of this preliminary study, the reactor was operated to emulate the first stage, lower temperature reaction. The inlet temperature would be moderated to about 225 °C by controlling the feeds and the outlet temperature would be allowed to achieve 285 °C. The pressure of the reactor was held at 50 psi.

Chlorination is an extremely exothermic reaction and it is practical to control the exotherm of reaction with a large excess of HF. A molar ratio of HF to hydrocarbon of ~30:1 effectively controlled the exotherm for the temperatures and feed rates of the examples. The patents recommend a chlorine to hydrocarbon molar ratio of 9–12:1 to ensure full chlorine-for-hydrogen exchange in the first reactor zone, but in practice, the chlorine feed could be nearly stoichiometric without any detrimental effects. Thorough dilution of the hydrocarbon and chlorine feeds in the HF is essential for minimizing by-product formation. As such, the HF feed was split into two equal streams. One stream was mixed with hydrocarbon and the other stream was mixed with chlorine. The two streams were vaporized each in a separate vaporizer. The two streams were recombined at the entrance to the reactor.

The Du Pont and the Great Lakes patents show that product composition may be changed by the choice of catalyst. For the preparation of saturated chlorofluoropropanes, catalysts based on iron, chromium or nickel are recommended. In verification studies on propene, chromium-based catalysts were found to be preferred. While iron based catalysts are reported to be more selective, excessive amounts of fragmentation of the C-3 chain into C-1 and C-2 compounds were observed with $FeCl_3$ on carbon.

2.2. Control experiments on propane and propene

With propane and propene feed rates of 0.25 mol/h, the 24 in. reactor provided sufficient residence time for complete chlorination, with no more than trace quantities of hydrogen-substituted material observed. While the reactor did produce some 2,2-dichloro-1,1,1,3,3,3-hexafluoropropane, **2**, mostly lesser-fluorinated materials were isolated. Trifluoro-, tetrafluoro- and pentafluoro-substituted chloropropanes were essentially the exclusive products for either feedstock, with tetrafluoro predominating. With yields of 90%, fluorine content was 67% of theoretical for $CF_3–CCl_2–CF_3$.

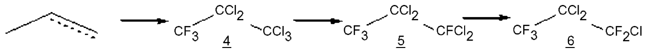
The Du Pont patent [1] indicates that the partially fluorinated intermediates in their process are almost all terminally fluorinated with 1,1,1-trifluoro substitution characteristic to each. This was verified in the products of both propane and propene, where under-fluorinated material of the formula was primarily 1,1,1,2,2-pentachloro-3,3,3-trifluoropropane, **4**. The under-fluorinated material of the formula $C_3F_4Cl_4$ was primarily 1,1,2,2-tetrachloro-1,3,3,3-tetrafluoropropane, **5** (isomer **5a** in Table 1). The under-fluorinated material of the formula $C_3F_5Cl_3$ was primarily 1,1,1,3,3-pentafluoro-2,2,3-trichloropropane, **6**. The cascade for fluorination into these isomers is shown in Scheme 3.

2.3. Experiments on propyne and propadiene

The application of high temperature chlorofluorination technology to acetylenes such as propyne is not a given. At the

Table 1
GC percentage of chlorofluoropropanes from chlorofluorination of C-3 hydrocarbons

Isomer formula	Isomer	Isomer structure	Propane product (%)	Propene product (%)	Propyne product (%)	Propadiene product (%)
$C_3F_4Cl_4$	**5a**	$CF_3–CCl_2–CFCl_2$	98	90.6	17.1	17.2
	5b	$CF_2Cl–CFCl–CFCl_2$	1	6.0	10.4	14.6
	5c	$CF_2Cl–CCl_2–CF_2Cl$	<1	<1	nd	nd
	5d	$CFCl_2–CF_2–CFCl_2$	nd	3.4	72.2	68.0



Scheme 3.

outset of these experiments, there were grave concerns as to the efficacy and the safety of such a reaction. Alkynes, themselves, are somewhat unstable. Acetylene, for example, is shipped as a solution in acetone as it is prone to detonation in the pure form. Acetylene, of course, is commonly used as a welding fuel. Propyne, in its role as a welding fuel, is sold diluted with propane and/or propene. Chloroacetylenes, especially small molecule fluorinated chloroacetylenes, are very unstable and detonate upon isolation. As high temperature chlorofluorination invariably proceeds through a series of partially chlorinated and fluorinated species, there were concerns about the possible generation of chloroacetylenic intermediates and safety of the proposed process. One can further diminish the prognosis for success when one takes into account the possibility of polymerization or carbonization of the propyne or olefinic intermediates onto the surface of the catalyst. Experimentation would prove that none of these concerns were to be any barrier to performing chlorofluorination reactions on propyne (or propadiene). Both C_3H_4 isomers underwent high temperature vapor phase chlorofluorination exceedingly well under the conditions developed in the control experiments.

Propyne was fed into the chlorofluorination reactor under the same conditions used to chlorofluorinate propane and propene. With an HF:Cl_2:propyne molar ratio of 30:10:1, the reaction ran adiabatically and the temperature of the inlet reactor zone stabilized around 230 °C. The second, higher temperature, reactor zone required some input of heat but was maintained at 285 °C. Total product yield was identical to chlorofluorination of propane and propene with 70% of product being $C_3F_4Cl_4$. Yield of liquid products was 91% with 64% fluorination. Analysis of non-condensed products mid-run showed them to be 94% $C_3F_6Cl_2$, $C_3F_5Cl_3$ and $C_3F_4Cl_4$ isomers. The fluorine content of the product mixture was the same as product from propane and propene, however the isomeric ratios for the various fluorinated materials were markedly different than those observed in the chlorofluorination of propane and propene. Table 1 shows the isomeric composition of the major, tetrafluorinated fraction.

It is clear that the selectivity for fluorination has reversed. Whereas propane and propene generate terminally fluorinated product (specifically, 1,1,1-trifluorinated), propyne produces product that is internally fluorinated, with a selectivity toward *gem*-difluorinated product.

In the above experiment, 98% pure propyne was used. The allenic isomer of propyne is 1,2-propadiene. Arimura et al. fluorinated and chlorofluorinated propadiene with chlorine monofluoride in the presence of cesium fluoride. 1-Chloro-2,2,3-trifluoropropane was the major product [5]. In light of the successful chlorofluorination of propyne, it was logical to investigate whether propadiene was as ameneable a reagent as was propyne and to determine whether the selectivity would remain the same. Under identical conditions to the above experiments, propadiene was fed to the chlorofluorination reactor. The reaction ran smoothly and chlorofluorinated products were obtained in 76% yield. The product composition was 7% $C_3F_5Cl_3$, 79% $C_3F_4Cl_4$ and 13% $C_3F_3Cl_5$. Selectivity was again high for *gem*-difluorinated product (see Table 1).

Future studies are planned to increase the level of fluorination to primarily $C_3F_5Cl_3$ isomers as well as decrease the level to $C_3F_3Cl_5$ so as to determine the isomeric ratios at those levels of fluorination. For the chlorofluorination of propyne and propadiene, it is clear that a change in the selectivity of early fluorination is occurring, and it is possible that this occurs before chlorination is complete. Currently, no monofluoro- or difluoro-intermediates have been isolated. Insight into the early selectivity of chlorofluorination would certainly shed light onto the selectivity for the tri-, tetra- and pentafluorinated species. Only additional study will reveal whether the early intermedates are mono- and difluorochloropropanes or mono- and difluorohydrochloropropanes.

3. Conclusions

Despite the potential for serious side reactions, propyne and propadiene have proven to be quite amenable to high temperature vapor phase chlorofluorination. The yield and extent of fluorination is nearly identical to that of propane and propene. However, propyne and propadiene show a selectivity for forming *gem*-difluoro substituted products, in contrast to the selectivity shown by propane or propene for forming terminal trifluoromethyl groups under these conditions.

4. Experimental

4.1. General

Anhydrous hydrogen fluoride was Matheson–Trigas CP grade. Chlorine was Matheson–Trigas HP grade. Propyne was 98% pure from Sigma–Aldrich. Propadiene was 96% from Synquest. Iron based catalyst was prepared by treating commercial carbon support pellets with saturated aqueous $FeCl_3$ hexahydrate as per Ref. [4], Example 1. Chromium based catalyst was prepared as per Ref. [4], Example 2, using a chromium oxide rather than chromium chloride solution. Chromium oxide was Baker ACS grade. GC/MS was performed on an HP 5890/5971A spectrometer with a 60M DB-1 capillary column. Chemical shifts of ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in ppm downfield from Me_4Si (δ 0.00) in $CDCl_3$ using a Bruker ARX300 instrument. ^{19}F NMR (282 MHz) were recorded in ppm downfield from internal standard $CFCl_3$ (δ 0.00) in $CDCl_3$. Hydrogen fluoride was pumped directly and the flow monitored by loss of mass from the feed cylinder. Chlorine and hydrocarbons were flowed as vapor through a rotameter and the flow monitored by loss of mass from the feed cylinder.

Cautionary note. Anhydrous HF causes severe burns to the skin and mucous membranes. HF should be handled with full PPE protection. An ample supply of HF antidote gel should be kept on hand before handling HF. See the reference for burn treatment procedures [6].

4.2. Typical catalyst bed preparation

The reactor constituted a 1 in. (2.54 cm) diameter nickel alloy tube 24 in. (61 cm) in length fitted with a five-point thermocouple running through the center of the reactor. Pressure control was achieved with a teflon diaphram gas regulator valve at the outlet end a vertical chilled water condenser. The reactor was charged with catalyst and purged with N_2 at 200 °C until no water vapor was detectable at the outlet with a cold mirror. Anhydrous hydrogen fluoride was then introduced at 1 mL/min for 1 h. The temperature was raised to the anticipated reaction temperature for 1 h. The N_2 stream was enriched to 2% O_2 for 2 h. The oxidant flow was stopped and the temperature stabilized to the desired reaction temperature. At the beginning of each reaction, anhydrous hydrogen fluoride was flowed at 70 g/h through the previously activated catalyst bed, maintaining an inlet reactor section temperature of 220 °C and an outlet reactor section temperature of 285 °C. A backpressure of 50 psi was allowed to build. After 0.5 h, a second HF flow was started at 70 g/h.

4.3. Chlorofluorination of propane

Into the first HF stream, propane was flowed at 9.8 g/h. Into the second HF stream, chlorine was flowed at 187 g/h. The temperature at the first thermocouple stabilized at about 230 °C. The temperature of the second thermocouple remained at 285 °C. The overall HF:Cl_2:propane ratio for the reaction was 31:12:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 10.4% $C_3F_5Cl_3$, 83.9% $C_3F_4Cl_4$ and 5.6% $C_3F_3Cl_5$.

4.4. Chlorofluorination of propene

Into the first HF stream, propene was flowed at 10.6 g/h. Into the second HF stream, chlorine was flowed at 197 g/h. The temperature at the second thermocouple stabilized at about 236 °C. The temperature of the last thermocouple stabilized at 291 °C. The overall HF:Cl_2:propene ratio for the reaction was 30:11:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 6.4% $C_3F_5Cl_3$, 78.5% $C_3F_4Cl_4$ and 13.5% $C_3F_3Cl_5$.

4.5. Chlorofluorination of propyne

Into the first HF stream, propyne was flowed at 8.7 g/h. Into the second HF stream, chlorine was flowed at 193 g/h. The temperature at the first thermocouple stabilized at about 236 °C. The temperature of the last thermocouple stabilizeded at 295 °C. The overall HF:Cl_2:propyne ratio for the reaction was 35:12:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 14.4% $C_3F_5Cl_3$, 69.5% $C_3F_4Cl_4$ and 6.9% $C_3F_3Cl_5$.

4.6. Chlorofluorination of propadiene

Into the first HF stream, propadiene was flowed at 8.1 g/h. Into the second HF stream, chlorine was flowed at 163 g/h. The temperature at the third (middle) thermocouple stabilized at about 226 °C. The temperature of the last thermocouple stabilized at 295 °C. The overall HF:Cl_2:propyne ratio for the reaction was 33:11:1. The outflow stream was condensed and collected under pressure and upon completion of the reaction, passed into crushed ice and separated. The clear, colorless liquid product was analyzed by gas chromatography. Product composition was 7.2% $C_3F_5Cl_3$, 78.5% $C_3F_4Cl_4$ and 13.0% $C_3F_3Cl_5$.

4.7. Spectral data (see Refs. [7–9] for literature values)

4.7.1. 1,1,2,2-Tetrachloro-1,3,3,3-tetrafluoropropane, **5a** ($CFCl_2$–CCl_2–CF_3)

^{19}F NMR (282 MHz, $CDCl_3$): δ −60.5 (q, J = 13.7, 1F, $CFCl_2$), −71.0 (d, J = 13.7, 3F, CF_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.5 (dq, J = 38.9, 29.8 Hz, CCl_2), 119.4 (d, J = 307.6 Hz, $CFCl_2$), 121.2 (q, J = 286.3 Hz, CF_3); MS *e/z* (%): 217 (100), 147 (13), 101 (20); 69 (100).

4.7.2. 1,1,2,3-Tetrachloro-1,2,3,3-tetrafluoropropane, **5b** ($CFCl_2$–CFCl–CF_2Cl)

^{19}F NMR (282 MHz, $CDCl_3$): δ −60.5 (q, J = 13.7, 1F, $CFCl_2$), −64.1 (ddd, J = 21.3, 16.0, 9.9, 1F, CFCl), −121.1 (ddd, J = 16.0, 12.2, 3.8, 1F, $CFCl_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 108.5 (dq, J = 271.5, 30.7 Hz, CFCl), 117.5 (dt, J = 312.0, 28.4 Hz, CF_2Cl), 124.9 (dt, J = 304.0, 34.5 Hz, CF_2Cl); MS *e/z* (%): 217 (15), 132 (14), 101 (80); 85 (100).

4.7.3. 1,2,2,3-Tetrachloro-1,1,3,3-tetrafluoropropane, **5c** (CF_2Cl–CCl_2–CF_2Cl)

^{19}F NMR (282 MHz, $CDCl_3$): δ −58.6 (s, 4F, CF_2Cl); ^{13}C NMR (75 MHz, $CDCl_3$): δ ~88.4 (hidden, CCl_2), 126.2 (t, J = 304.7 Hz, CF_2Cl).

4.7.4. 1,1,3,3-Tetrachloro-1,2,2,3-tetrafluoropropane, **5d** ($CFCl_2$–CF_2–$CFCl_2$)

^{19}F NMR (282 MHz, $CDCl_3$): δ −66.6 (t, J = 6.3, 2F, $CFCl_2$), −108.7 (t, J = 6.3, 2F, CF_2Cl), ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.7 (tt, J = 271.8, 29.9 Hz, CF_2), 114.7 (dt, J = 307.4, 36.4 Hz, $CFCl_2$); MS *e/z* (%): 217 (16), 147 (9), 116 (46); 101 (100); 85 (40); 66 (50).

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