Dehydrohalogenation of 1,1,1-Trihaloethanes

FRANCIS H. WALKER AND ATTILA E. PAVLATH

Richmond Research Center, Stauffer Chemical Company, Richmond, California

Received March 4, 1965

During the course of our investigation of the preparation of fluorinated olefins, a number of metal oxides were found which catalyzed the dehydrohalogenation of 1,1,1-trifluoroethane and 1,1,1-difluorochloroethane at temperatures of 200–400°. Both dehydrochlorination and dehydrofluorination were observed according to the catalyst employed. Several catalysts were found to be selective, favoring one or the other reaction, depending upon the reaction temperature.

The dehydrohalogenation of haloalkanes by bases usually occurs quite readily in the liquid phase. Pentachloroethane[1] and heptachloropropane,[2] for example, give the corresponding olefins in high yields and conversions when treated with alcoholic or aqueous caustic solutions. In the case of chlorofluoroalkanes, the reaction is selective: dehydrochlorination is claimed exclusively.[3–5] The temperature required is generally above 30°. This limits the application of this method in practice to those chlorofluoroalkanes which have boiling points of 60° or higher in order to avoid losses of starting material. More volatile compounds, as well as those boiling above 60°, can be dehydrohalogenated thermally. Highly chlorinated chlorofluoroethanes (*e.g.*, CCl_2FCCl_2H[6]) will eliminate hydrogen chloride easily with or without a catalyst. The conversion and yield depends upon the structure of the haloalkane. In general, lower yields are obtained when more than one hydrogen atom is present in the molecule, because in this case further dehydrohalogenation can take place.[7] At 910°, for example, 1,1,1-trifluoroethane was found to give more than the stoichiometric amount of acid.[8]

The boiling point of the alkene formed by the elimination of hydrogen fluoride from a chlorofluoroalkane is about the same as that of the parent compound (Table I). This fact has made it difficult in the past to determine the extent of dehydrochlorination, since dehydrofluorination might have gone undetected. Some dehydrofluorinated product could be included in the amount of "recovered starting material." In the present work, product composition was readily determined by gas chromatography on a di-*n*-butyl maleate column.

TABLE I

BOILING POINTS OF CHLOROFLUOROALKANES AND THE CORRESPONDING ALKENES DERIVED BY DEHYDROFLUORINATION

Alkane	B.p., °C.	Alkene	B.p., °C.
$CF_2ClCHCl_2$	71.9	$CFCl{=}CCl_2$	71.0
$CFCl_2CH_2Cl$	88	$CCl_2{=}CHCl$	87
$CFCl_2CH_3$	32	$CCl_2{=}CH_2$	37
$CFCl_2CHCl_2$	116.6	$CCl_2{=}CCl_2$	121

Pyrolysis of 1,1,1-difluorochloroethane at 870° has been shown previously to give a mixture of 1,1-difluoroethylene and 1-chloro-1-fluoroethylene.[9] Similarly, at temperatures of 600 to 1000°, 1,1,1-trifluoroethane will undergo elimination of hydrogen fluoride to give 1,1-difluoroethylene.[8] The temperature at which dehydrohalogenation occurs can be reduced considerably by employing catalysts. For example, hydrogen fluoride is eliminated from 1,1,1-difluorochloroethane at 250–400° when it is passed over aluminum fluoride or aluminum oxide.[10,11] Dehydrochlorination of 1,1,1-difluorochloroethane occurs at 600° when copper is used as a catalyst.[12] At lower temperatures 1,1,1-dichlorofluoroethane will eliminate hydrogen fluoride when it is passed through a nickel tube, but the yield is substantially lower.[13]

Results and Discussion

We have extended the investigation of the thermal dehydrohalogenation of 1,1,1-trihaloethanes by employing a number of different catalysts with both 1,1,1-difluorochloro (I) and 1,1,1-trifluoroethane (II). We found that, depending on the catalyst and/or the applied temperature, both dehydrochlorination and dehydrofluorination can be accomplished in good yield and conversion under 400°. It is convenient to group these catalysts into different classes. In the first class are those which catalyzed the dehydrochlorination of I with some dehydrofluorination (Table II).

TABLE II

VAPOR PHASE DEHYDROHALOGENATION OF 1,1,1-DIFLUOROCHLOROETHANE

Catalyst	Temp., °C.	$CF_2{=}CH_2$, %	$CFCl{=}CH_2$, %
NiO	300	64.0	14.4
	400	99.4	0.4
Fe_2O_3	300	43.3	2.6
	400	95.8	0.3
ZnO	300	...	...
	400	96.1	3.5
Ag	300	...	...
	400	64.4	5.6
None	500	5.9	...

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Our investigation has shown the catalysts in the first class to be quite selective. Whereas at 400° with I they give dehydrochlorination, at the same temperature with II all of them (with the exception of silver) effect dehydrofluorination in good conversion (Table III). Dehydrofluorination was less than 0.1% at 300°.

TABLE III
DEHYDROFLUORINATION OF 1,1,1-TRIFLUOROETHANE AT 400°

Catalyst	Conversion, %
NiO	59.1
Fe_2O_3	30.2
ZnO	63.4
Ag	5.7

The use of Al_2O_3 and SiO_2 resulted in dehydrofluorination with a small amount of dehydrochlorination. However, when a mixture of Al_2O_3 and SiO_2 (12.4 wt. % Al_2O_3 and 87.3 wt. % SiO_2) was used, the direction of the reaction depended upon the temperature employed. A similar temperature dependence was observed with TiO_2 (Table IV).

TABLE IV
DEHYDROHALOGENATION OF 1,1,1-DIFLUOROCHLOROETHANE

Catalyst	Temp., °C.	$CF_2{=}CH_2$, %	$CFCl{=}CH_2$ %
Al_2O_3	200	...	1.8
	300	1.3	91.0
	400	7.6	90.6
SiO_2	400	14.5	75.5
Al_2O_3–SiO_2	200	1.1	52.2
	300	36.6	63.2
	400	78.6	2.1
TiO_2	300	2.0	88.0
	400	67.2	11.8
AlF_3–Al_2O_3	300	10.4	79.5
	400	12.4	83.4
Activated charcoal	300	93.5	3.2
None	500	5.9	...

The analysis of the oxides after use indicated that only 5-10% of the HF or HCl which formed reacted with the catalyst. The dehydrohalogenation observed with the activated charcoal of high surface area also shows that it is a surface reaction and not a chemical reaction between the metal oxides and the 1,1,1-trihaloethane. Additional evidence is shown by the fact that molten KOH or NaOH gave less than 1% dehydrohalogenation under similar reaction conditions.

Experimental Section

Materials.—The 1,1,1-trifluoroethane and the 1,1,1-difluorochloroethane were prepared by the fluorination of 1,1,1-trichloroethane using arsenic trifluoride with antimony pentachloride as catalyst.[14]

Catalysts.—The hard alumina (Houdry Grade 200, 98.5 wt. % Al_2O_3) and the synthetic silica–alumina catalyst (Houdry Grade S-90, 12.4 wt. % Al_2O_3 and 87.3 wt. % SiO_2) were obtained from the Houdry Process Corp., Chemicals Division. The silver catalyst (Harshaw Ag-0101E $^1/_8$ in., 3.5–4.0 wt. % silver on an inert alumina support), the zinc oxide catalyst (Harshaw ZN-0101T $^1/_8$ in.), and the titania catalyst (Harshaw Ti-0102T $^1/_8$ in.) were obtained from the Harshaw Chemical Co. The ferric oxide (Girdler G-42, 0.25-in. tablets) and the nickel oxide (Girdler T-311, 4–6 wt. % NiO on an inert alumina support) catalysts were obtained from Girdler Catalysts, Chemical Products Division, The Chemetron Corp. The activated charcoal (Barnebey-Cheney, 4–6 mesh, 600–700 m.^{2}/g.) was obtained from the Barnebey-Cheney Co. The silica gel catalyst (Davison Grade 70, mesh size 10) was obtained from W. R. Grace and Co., Davison Chemical Division. The AlF_3–Al_2O_3 catalyst was prepared in our laboratory by passing anhydrous HF over Al_2O_3 at 500°. Analysis showed 8.2% fluorine (12.1% AlF_3).

General Procedure for the Dehydrohalogenation Reactions.—A Monel tube (1.5-cm. inside diameter, 50 cm. long) was filled with catalyst and heated over a 30-cm. section by an electric tube furnace. The catalyst was purged with nitrogen (200 cc./min.) for 15 min. at reaction temperature before use to remove any volatile impurities. The 1,1,1-difluorochloroethane or 1,1,1-trifluoroethane was preheated to 120° and then introduced into the reaction tube at a rate such that the contact time was 30 sec. The products leaving the reactor were collected over water in a buret. This procedure removed the hydrogen chloride and/or hydrogen fluoride present and was found to be a convenient way of collecting the product for analysis by gas chromatography and infrared spectroscopy. The composition of the reaction product was established by gas chromatography using a 12 ft. × 0.25 in. column of di-*n*-butyl maleate at 40°. Each component was identified by its retention time compared with that of a known sample. The identity of the reaction product was established also by comparison of the infrared spectrum with those that are published in the literature for $CF_2{=}CH_2$[15] and $CFCl{=}CH_2$.[16]

Acknowledgment.—The authors wish to thank Mrs. Judy Young for the thorough literature research on dehydrochlorination of chlorofluoroalkanes.

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(14) This and similar fluorination reactions are to be reported in a separate paper.

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