Journal of Fluorine Chemistry, 13 (1979) 7 – 18

Received: October 19, 1978

CHEMISTRY IN HYDROGEN FLUORIDE V. CATALYSTS FOR REACTION OF HF WITH HALOGENATED OLEFINS‡

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SUMMARY

Tantalum pentafluoride, niobium pentafluoride, titanium tetrachloride, and molybdenum pentachloride catalyze the addition of hydrogen fluoride to tetra- and trichloroethene and related compounds. Hydrogenation of tetrachloroethene to 1,1,2,2-tetrachloroethane was observed using hydrogen, methylcyclopentane, and TaF_5 in HF.

INTRODUCTION

The liquid phase addition of hydrogen fluoride to alkenes is an important method for the synthesis of organofluorine compounds.[1] The addition proceeds readily with hydrocarbon alkenes at room temperature or below. Alkenes heavily substituted by halogen, such as tetra- or trichloroethene, require a catalyst, traditionally antimony pentachloride[2] or boron trifluoride.[3] In this report, several new catalysts for this addition are described, in particular, tantalum pentafluoride which appears to have major advantages over previously employed catalysts.

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‡ Contribution No. 2615

RESULTS

The fluorination of tetrachloroethene (**1**) formally involves two processes: addition of HF to the double bond to give the monofluorinated derivative **2** followed by a series of fluorine for chlorine exchange reactions giving the more highly fluorinated derivatives **3** and **4**. Catalysts for this process were screened

$$\underset{\mathbf{1}}{CCl_2{=}CCl_2} \xrightarrow[\text{catalyst}]{HF} \underset{\mathbf{2}}{HCCl_2{-}CCl_2F} \xrightarrow[\text{catalyst}]{HF}$$

$$\underset{\mathbf{3}}{HCCl_2{-}CClF_2} \xrightarrow[\text{catalyst}]{HF} \underset{\mathbf{4}}{HCCl_2{-}CF_3}$$

in a series of batch experiments. A mixture of 0.2 mole of **1**, 0.5 mole of HF, and 0.006 to 0.018 mole of the catalyst was heated at 75-150° in a closed vessel. After appropriate reaction time the mixture was cooled to 0° and quenched with ice water. The organic phase was separated, dried, and analyzed by glpc. The results are shown in Table 1. In all cases, examination of the crude reaction mixture by proton and fluorine nmr showed only absorptions assignable to the products in Table 1. Control experiments demonstrated that no reaction occurred in the absence of a catalyst.

The results indicate that TaF_5, $TiCl_4$, MoF_5, and NbF_5, in addition to the previously known $SbCl_5$, are active catalysts for the reaction. Tantalum pentafluoride appears to be the most active of the materials tested, maintaining its activity to temperatures as low as 75° where antimony pentachloride was inactive.

Table 1

Addition of HF to Tetrachloroethylene[a]

Catalyst (mole %)[b]	Temperature	Product Weight[c]	Product Analysis[d]			
			1	**2**	**3**	**4**
TaF_5 (9)	150°	24.9 g	3	4	93	-
TaF_5 (2.5)	150°	27.3 g	1	3	94	2
TaF_5 (9)	75°	30.3 g	30	40	30	-
$SbCl_5$ (3)	150°	24.6 g	48	21	30	-
$SbCl_5$ (9)	75°	28.7 g	100	-	-	-
$TiCl_4$ (9)	150°	25.9 g	47	42	11	-
$MoCl_5$ (9)	150°	22.8 g	32	53	16	-
NbF_5 (5)	150°	29 g	61	34	4	-

a. 0.2 mole $CCl_2=CCl_2$; 0.5 mole HF; 6 hr.

b. mole percent based on $CCl_2=CCl_2$.

c. crude product after washing with water, drying, and filtering.

d. by glpc using a 10 ft x 0.25 in. 10% carbowax column operated at 60°.

Under the conditions of these batch experiments, BF_3, $TaCl_5$, Ta_2O_5, CoF_3, V_2O_5, $ZrCl_4$, $NbCl_5$, HgO, and WCl_6 showed no catalytic activity at 150° for the addition reaction. A preparative scale experiment (Table 2, entry 6) using TaF_5 gave an 86% yield of pure distilled **3**.

Results on the fluorination of additional halogenated compounds using TaF_5 catalysis are shown in Table 2. Fluorotrichloroethene was smoothly converted to a mixture of **3** and **4** at 150°. Trichloroethene (**5**), a more sensitive molecule than tetrachloroethene, required somewhat different conditions for successful fluorination. Best results were achieved by adding the olefin to a stirred solution of TaF_5 in HF at relatively low temperatures (5-25°). HCl generated in the reaction must be

Table 2

Fluorination Reactions

Substrate (moles)	HF, moles	Catalyst (moles)	Conditions	Product (%)[a]
$CClF{=}CCl_2$ (0.2)	0.5	TaF_5 (0.018)	150°/6 hr	$HCCl_2\text{-}CClF_2$ (75) $HCCl_2\text{-}CF_3$ (15)
$CCl_2{=}CHCl$ (0.08)	0.25	TaF_5 (0.002)	25°/0.5 hr	$H_2CCl\text{-}CClF_2$ (32) $H_2CCl\text{-}CCl_2F$ (40) $H_2CCl\text{-}CCl_3$ (1)
$CCl_2{=}CHCl$ (0.8)	1.0	TaF_5 (0.008)	5°/2.5 hr	$H_2CCl\text{-}CCl_2F$ (89)
$CCl_2{=}CHCl$ (0.3)	0.5	BF_3 (0.015)	25°/17 hr	$H_2CCl\text{-}CCl_2F$ (33) recovered $HCCl{=}CCl_2$ (60)
$CH_2{=}CCl_2$ (0.4)	0.5	TaF_5 (0.01)	25°/3 hr	$H_3C\text{-}CCl_2F$ (40) tar
$CCl_2{=}CCl_2$ (0.8)	2.0	TaF_5 (0.02)	150°/6 hr	$HCCl_2\text{-}CClF_2$ (86)
$HCCl_2CCl_2F$ (0.2)	0.25	TaF_5 (0.018)	150°/6 hr	$HCCl_2\text{-}CClF_2$ (80) $HCCl_2\text{-}CF_3$ (10)
CH_3CCl_3 (0.25)	0.25	TaF_5 (0.0075)	75°/6 hr	$H_3C\text{-}CCl_2F$ (31) $H_3C\text{-}CClF_2$ (5)
$CH_2ClCClF_2$ (0.2)	1.0	TaF_5 (0.01)	100°/6 hr	$H_2CCl\text{-}CF_3$ (70)
$HCCl_2CCl_2H$ (0.2)	0.5	TaF_5 (0.018)	150°/6 hr	$H_2CCl\text{-}CF_3$ (trace) tar recovered $HCCl_2\text{-}CCl_2H$ (50)

a. Isolated yield of distilled product, based on substrate charged.

vented to prevent formation of substantial quantities of the HCl addition product, 1,1,1,2-tetrachloroethane. Under these conditions quite good yields of fluorinated products 6 and 7 were obtained. In contrast, under somewhat more severe conditions, the catalyst boron trifluoride[3] gave only a 33% yield of 6 with the remainder being unreacted 5.

$$\begin{array}{cccccc} HCCl{=}CCl_2 & \xrightarrow[\substack{TaF_5 \\ 25^\circ}]{HF} & H_2CCl{-}CCl_2F & \xrightarrow[TaF_5]{HF} & H_2CCl{-}CClF_2 & \xrightarrow[TaF_5]{HF} \\ \mathbf{5} & & \mathbf{6} & & \mathbf{7} & \end{array}$$

$$\begin{array}{c} H_2CCl{-}CF_3 \\ \mathbf{8} \end{array}$$

Vinylidene chloride gave 1,1-dichloro-1-fluoroethane in 40% yield when treated with TaF_5 and 1.25 equivalents of HF at 25°.

The fluorination of several saturated halocarbons using TaF_5/HF was briefly explored (Table 2). As expected, 2 was converted cleanly to 3 and 4 at 150°. Both 7 and 1,1,1-trichloroethane were fluorinated under relatively mild conditions. However, 1,1,2,2-tetrachloroethane gave mainly tars plus unreacted substrate when treated with TaF_5/HF at 150°.

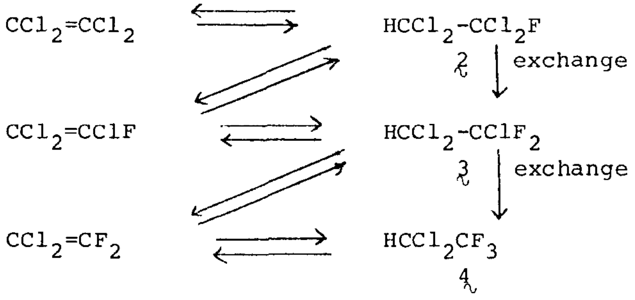
In view of the recent interest in acid catalyzed hydrogenation reactions,[4-7] a brief study on the reduction of 1 in the TaF_5/HF medium was conducted. The presence of hydrogen at pressures up to 5000 psi had no effect on the reaction of 1 with TaF_5/HF under the conditions of the first entry in Table 1. Reaction in the presence of 0.2 mole of methylcyclopentane, a potential hydride donor, resulted only in conversion of the hydrocarbon to cyclohexane; **1** was recovered unchanged. However, heating a mixture of tetrachloroethene (0.2 mole), HF (0.5 mole), TaF_5 (0.018 mole), methylcyclopentane (0.1 mole), and hydrogen (5000 psi) gave only traces of unreacted **1** and the fluorination products **2**, **3**, or **4**. The major product was 1,1,2,2-tetrachloroethane, isolated in 30% yield based on **1**. The methylcyclopentane was recovered essentially unchanged.

DISCUSSION

The addition of hydrogen fluoride to olefins is likely to involve protonation of the olefin followed by capture of the resulting cation by fluoride.[1] Catalysis of this process probably stems from the formation of more highly acidic species capable of protonating the weakly basic halogenated olefins. The formation of 'super-acid' systems from HF and fluoride ion acceptors such as antimony pentahalides and tantalum pentafluoride is well known.[8]

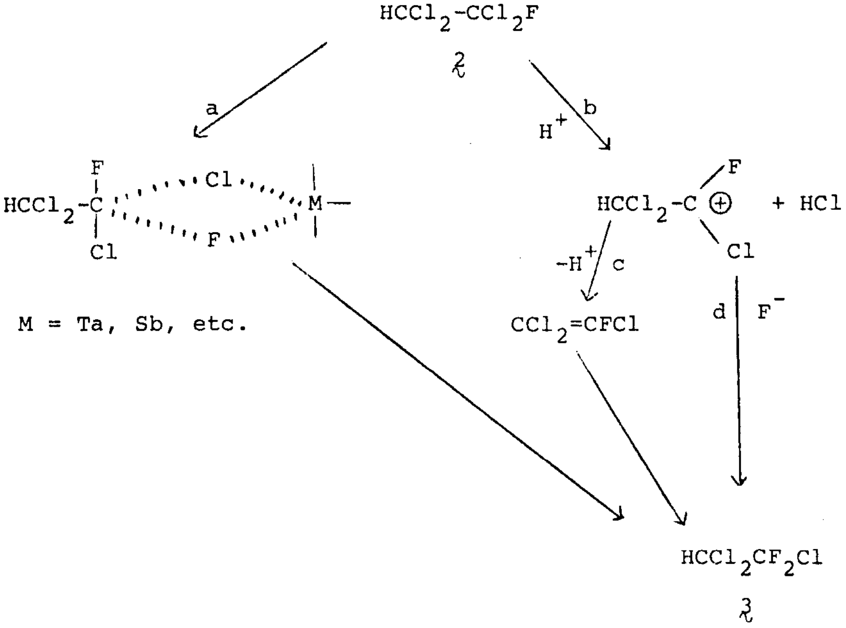
The mechanism of the subsequent formation of more highly fluorinated products, e.g., **3** and **4**, is more difficult to define. Both a direct exchange process and an elimination-addition sequence (Scheme 1) could account for the observed results.

Scheme 1



The conversion of 2 to 3 is a catalyzed process as no reaction occurs when 2 is treated with HF alone at 150°. *A priori*, several mechanisms for this catalysis can be proposed (Scheme 2). Pathway a is a ligand exchange process which has previously been proposed[9] for antimony halide catalyzed fluorination reactions.

Scheme 2



Pathway b involves an acid catalyzed loss of chloride generating a carbocation which can form product through the olefin (pathway c) or directly by fluoride ion capture (pathway d). The requirements for any active catalyst for these processes should differ. The effectiveness of a catalyst for the direct exchange process (pathway a) should depend in part on the lability of its ligands and the concentration of coordinately unsaturated species in solution. Pathway b requires the catalyst to generate a species sufficiently acidic to protonate 2. In principle, a comparison of the efficiency of the various catalysts identified in this study for the **1** ——> **2** transformation compared to the **2** ——> **3** process could provide information on these mechanistic possibilities Unfortunately, interpretations of data from this study is complicated by the question of relative catalyst lifetimes. In fact, the superior performance of TaF_5 observed here may derive largely from its greater resistance to reduction[6] compared with antimony halides.[10] Reduction of Sb(V) to Sb(III) is known[5] to decrease its activity as a fluorination catalyst.

The reduction of **1** to 1,1,2,2-tetrachloroethane is another example of the now well known[4-6] reduction of carbocations in superacid media. Interestingly, the cation produced by protonation of **1** is not directly reduced by H_2, but is efficiently reduced in the presence of a hydrocarbon capable of donating hydride from a tertiary position, behavior similar to that of delocalized carbocations formed by the protonation of aromatic hydrocarbons.[4]

EXPERIMENTAL

Hydrogen fluoride (Air Products), tantalum pentafluoride (Alfa), niobium pentafluoride (Alfa), titanium tetrachloride (Fisher), and molybdenum pentachloride (Alfa) were used as received. Antimony pentachloride (B & A) was distilled in an inert atmosphere before use. All other reagents were commercial samples used as received. Proton NMR spectra were obtained on a Varian A-60 instrument in $CDCl_3$ with TMS as internal standard. Fluorine NMR spectra were obtained on a Varian XL-100 instrument operated at 94.1 MHz using $CFCl_3$ as internal standard. Glpc data were obtained on a Hewlett-Packard 5700A instrument.

Caution! Hydrogen fluoride is extremely corrosive to human tissue, contact resulting in painful, slow-healing burns. Laboratory work with HF should be conducted only in an efficient hood with operator wearing full face shield and protective clothing.

Catalyst Screen

An 80-ml Hastelloy bomb tube was charged with 33.2 g (0.2 mole) of tetrachloroethene and 0.018 mole of the catalyst. The bomb was cooled in dry ice and acetone, evacuated, and charged with 10 g (0.5 mole) of hydrogen fluoride, and brought to atmospheric pressure with nitrogen. The bomb was agitated for six hours with an inside temperature of 150°C. The bomb was cooled in ice water and the contents were discharged onto 30 g of ice, using 40 ml of water to rinse the bomb. The lower organic layer was collected, washed with water, and dried over anhydrous calcium chloride. The material was weighed and analyzed by gas liquid chromatography against authentic comparison samples using a 10 ft x 0.25 in 10% Carbowax column with an oven temperature of 60°C and a helium carrier gas flow of 60 ml/min. The results are contained in Table 1.

Preparation of 1,2,2-Trichloro-1,1-Difluoroethane (**3**)

A 360-ml Hastelloy bomb tube was charged with 132.8 g (0.8 mole) of tetrachloroethene and 5.6 g (0.02 mole) of tantalum pentafluoride. The bomb was cooled in dry ice and acetone, evacuated, and charged with 40 g (2 mole) of hydrogen fluoride. The bomb was agitated for 6 hr with an inside temperature of 150°C. The bomb was cooled in ice water, and the contents were discharged onto 50 g of ice using 75 ml of water to rinse the bomb. The lower organic layer was separated, washed with water, and dried over calcium chloride. It weighed 126.5 g. A 115.6-g portion of the product was distilled at atmospheric pressure to give 104.6 g (0.675 mole, 84%) of 1,2,2-trichloro-1,1-difluoroethane as a colorless liquid, bp 70-72°C; proton NMR (δ, $CDCl_3$) 5.85 (t, J = 5.3 Hz); fluorine NMR (δ, $CDCl_3$) -63.31 (d, J = 5.3 Hz).

Preparation of 1,1,2-Trichloro-1-Fluoroethane (**6**)

A 250-ml polychlorotrifluoroethylene vessel was charged with 2.2 g (0.008 mole) of tantalum pentafluoride. The vessel was evacuated, cooled in liquid N_2 and charged by distillation with 20 g (1.0 mole) of hydrogen fluoride. The vessel was filled with nitrogen and immersed in a bath of water and ethylene glycol at 5°C. Trichloroethene (108 g, 0.8 mole), cooled to 0°C, was added in one portion. The resulting mixture was stirred for 2.5 hr. The mixture was poured over 40 g of cracked ice. The organic layer was separated, washed with water, and dried over anhydrous calcium chloride. It weighed 116.7 g. 1,1,2-Trichloro-1-fluoroethane (108.1 g, 89%), bp 87-89°C, was obtained by distillation; proton NMR (δ, $CDCl_3$) 4.13 (d, J = 13 Hz)

Hydrogenation of Tetrachloroethene

An 80-ml Hastelloy bomb tube was charged with 33.2 g (0.2 mole) of tetrachloroethene, 8.4 g (0.1 mole) of methylcyclopentane, and 2.8 g (0.01 mole) of tantalum pentafluoride. The bomb was cooled in dry ice and acetone, evacuated and charged with 10 g (0.5 mole) of hydrogen fluoride. The bomb was warmed to 25° and pressured to 5000 psi with hydrogen. The bomb was agitated for 6 hr with an inside temperature of 150°C. The bomb was cooled to 0° and vented slowly to atmospheric pressure. The contents were discharged onto 40 g of ice. The lower organic layer was collected, washed with water, and dried over anhydrous calcium chloride. Evaporative distillation of the material at 2 mm to a vessel cooled in dry ice gave 19 g of colorless liquid, separating it from a quantity of tar. Proton NMR of the liquid showed upfield absorption for methylcyclopentane and a singlet at δ 5.95 for 1,1,2,2-tetrachloroethane. Glpc analysis of the material against authentic samples using a 10 ft x 0.25 in 10% carbowax column with an oven temperature of 50° confirmed the above products. The chromatograph also showed traces of **1**, **2**, and **3**.

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