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The reactions of xenon difluoride with 'inert' solvents*

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Abstract

The reactions of XeF_2 with a variety of organic solvents are described. XeF_2 is found to undergo both hydrogen– and chlorine–fluorine exchange over a relatively short timescale with chloroform, dichloromethane and dibromomethane. XeF_2 reacts very slowly with tetrachloromethane and fluorotrichloromethane, although the addition of a catalytic amount of HF increases the rate of reaction considerably. XeF_2 dissolves in acetonitrile with negligible reaction to the extent of 2.25 mol kg^{-1}.

Introduction

Xenon fluorides, especially XeF_2, have been shown to be efficient, convenient and specific fluorinating agents for a wide range of organic [1] and inorganic [2] compounds. Many of these reactions have been moderated by dissolving the substrates in 'non-reactive' solvents such as hydrochlorocarbons, allowing mechanistic studies to be carried out which suggest that HF_2^- and XeF^+ are important intermediates [3]. However, since the free fluoride anion abstracts a proton from CH_3CN and undergoes halogen-exchange reactions with hydrochlorocarbons at room temperature [4], we have investigated the reactions of xenon difluoride with a range of organic solvents to investigate whether these solvents can really be considered to be inert.

Experimental

XeF_2 was prepared by the literature route [5]. The solvents were extensively purified and dried before use by washing with acid, water, base, water, drying over $CaCl_2$ and P_2O_5, distilling on a Spaltrohr under dry argon and then vacuum distilling on to the appropriate molecular sieves for storage in the dark.

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Analysis of the reactions was carried out by ^{1}H and ^{19}F NMR spectroscopies on a Bruker AM300 NMR spectrometer at 300.13 and 282.4 MHz respectively with a 5 mm bore selective probe. In a typical experiment, XeF_2 was charged into a pre-fluorinated 4 mm o.d. (0.5 mm wall thickness) FEP tube (Production Techniques Ltd., Fleet, Hampshire, UK) in a dry box. The XeF_2 was held at −196 °C while the tube was evacuated to high vacuum, dry solvent was distilled into the tube under static vacuum and the tube allowed to warm to room temperature for the desired time (see Table 1) with occasional venting to remove xenon gas thus affording a pale yellow solution. The reaction tube was then cooled to −196 °C and sealed at an appropriate length by means of an electrical resistive circular heater. The sealed tube was placed in a precision 5 mm NMR tube with acetone-d_6 and CF_3CH_2OH ($\approx$33% v/v) in a film between the two tubes as a deuterated lock substance and to allow direct ^{19}F versus ^{1}H integrations, respectively. The solubility of XeF_2 in the solvents was estimated by ^{19}F and ^{1}H NMR spectroscopies.

Results and discussion

Xenon difluoride was found to react with a number of solvents which were previously believed to be inert to XeF_2. The products, yields and reaction times are given in Table 1.

Fourier-transform NMR spectroscopy is a convenient technique for trace analysis providing extreme care is taken in field homogenization, shimming, baseline subtraction and integration. Since we have shown that XeF_2 reacts

TABLE 1. Reactions of XeF_2 with hydrohalogenocarbons at room temperature

Organic solvent	CH_2Cl_2	$CHCl_3$	CCl_4	$CFCl_3$	CH_2Br_2	$CFCl_2CF_2Cl$
Weight[a]	0.5261	0.5817	0.6299	0.5000	0.9453	0.7031
	(6.19)	(4.86)	(4.09)	(4.07)	(5.40)	(3.75)
Weight of XeF_2[b]	48.8	19.4	19.2	19.8	19.6	53.6
	(0.289)	(0.115)	(0.114)	(0.117)	(0.116)	(0.317)
Time	2 d	2 d	20 d	14 d	5 min	20 d
Organic products formed[c]						
CH_2FCl	24.4	–	–	–	–	–
$CHFCl_2$	25.6	67.1	–	–	–	–
CH_2F_2	0.4	–	–	–	16.5	–
CHF_2Cl	0.3	1.2	–	–	–	–
CF_2Cl_2	0.1	–	20.6	89.2	–	22.2
$CFCl_3$	0.2	13.9	78.3	–	–	–
CF_3Cl	–	–	1.1	11.8	–	2.5
CH_2FBr	–	–	–	–	76.9	–
$CHFBr_2$	–	–	–	–	3.3	–
HF	37.0	17.8	–	–	3.3	

[a] Weight in grammes (no. of mmoles in parentheses).
[b] Weight in mg (no. of mmoles in parentheses).
[c] In mol.%.

with a range of solvents, it was essential that mixed-solvent systems were avoided. The technique of sealing the reagents in a 4 mm o.d. tube and placing this tube inside a 5 mm o.d. tube containing a suitable deuterated solvent satisfied our requirements, but shimming on the solvent in the 4 mm tube was now essential. The provision of a small quantity of a solvent containing both fluorine and hydrogen, in this case 2,2,2-trifluoroethanol, CF_3CH_2OH, in the 5 mm tube, allowed a reliable integration of ^{19}F against ^1H NMR signals, particularly for hydrogen-containing non-fluorinated solvents.

The results listed in Table 1 illustrate that XeF_2 can undergo both chlorine- and hydrogen-exchange reactions with hydrohalocarbons at room temperature. Careful purification and drying of all the solvents was also essential. The reaction of XeF_2 with poorly dried or impure dichloromethane could be violently explosive below room temperature under our conditions. Despite the relative C—Cl bond strengths, XeF_2 reacts with CCl_4 significantly slower than with $CHCl_3$ or CH_2Cl_2. However, the addition of a small amount of HF (*c.* 1 μmol) catalysed the reaction with CCl_4 to completion, as shown by the absence of peaks due to XeF_2 in the ^{19}F NMR spectrum within 1 h, while the selectivity remained unaffected. In the absence of HF, the solubility of XeF_2 in CCl_4 was 0.076 mol kg^{-1}. In the presence of HF, XeF_2 is believed to behave like an electrophile. The weak coordination of CCl_4 to xenon would polarise the C—Cl bond, facilitating chlorine/fluorine exchange. The weak coordination of chlorocarbons to electron-deficient metal centres has already been noted [6], and has been invoked to account for chlorine/fluorine-exchange reactions between some binary transition-metal fluorides [7] or transition-metal oxide fluorides [8] and hydrochlorocarbons.

The by-products, xenon—chloro complexes, have not been observed, but this is not surprising since xenon—chlorine species are generally unstable except at very low temperatures. Decomposition would thence give xenon and chlorine, the latter resulting in the observed yellow colouration of the NMR samples. Fluorocarbons [e.g. $CFCl_3$, Arcton 113 ($CF_2ClCFCl_2$), Arcton 133a (CF_3CH_2Cl)] are less electrophilic [6, 9], and therefore react with XeF_2 even slower than CCl_4. The addition of a catalytic amount of HF to the reaction of XeF_2 with $CFCl_3$ allowed the reaction to go to completion in a few hours, but had no catalytic effect on the reactions of XeF_2 with Arcton 113 or 133a. For Arcton 113, there was no appreciable chlorine/fluorine exchange after 20 d at room temperature; greater than 90% of the XeF_2 remained unreacted and the only identifiable products were the C—C bond-cleavage products, CF_2Cl_2 and CF_3Cl. There was no reaction between XeF_2 and Arcton 133a after 1 year at room temperature. In the absence of HF, the solubility of XeF_2 in $CFCl_3$, Arcton 113 and Arcton 133a was 0.51, 0.11 and 1.46 mol kg^{-1}, respectively.

In the reactions of XeF_2 with CH_2Cl_2 and $CHCl_3$, both chlorine/fluorine and hydrogen/fluorine exchanges were observed. In the $XeF_2 + CH_2Cl_2$ reaction, 24% $CHCl_3$ was also generated. Hydrogen exchange affords HF which would then autocatalyze the chlorine/fluorine-exchange mechanism. This hydrogen/fluorine exchange, which is also observed from the reactions of d^0 transition-metal fluorides with hydrohalocarbons, occurred via a radical process which accounts for the generation of $CHCl_3$.

When the C–X bond is weakened, as in the reaction of XeF_2 with CH_2Br_2, almost exclusive bromine/fluorine exchange occurred within 5 min. XeF_2 underwent only a very slow reaction with CH_3CN. After 6 weeks, only traces (<4 mol%) of HF and CFH_2CN could be observed. The solubility of XeF_2 in pure CH_3CN was determined as 2.25 mol kg^{-1} CH_3CN (1.77 mol l^{-1} CH_3CN).

Conclusions

Although dichloromethane and chloroform may be suitable solvents for quick XeF_2 fluorinations of organic and inorganic molecules, this work has shown that XeF_2 may fluorinate the solvent, affecting reaction stoichiometries and more importantly producing HF, the role of which in these reactions is unclear. Further investigations into the mechanisms of these reactions are underway. For kinetic studies and slow reactions, CH_3CN or fluorochlorocarbons might be more appropriate 'inert' solvents.

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