# The reactions of xenon difluoride with 'inert' solvents*

Wolfgang W. Dukat, John H. Holloway†, Eric G. Hope, Paul J. Townson
*Department of Chemistry, The University, Leicester LE1 7RH (UK)*

Richard L. Powell
*ICI Chemicals and Polymers, The Heath, Runcorn, Cheshire (UK)*

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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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†Author to whom correspondence should be addressed.

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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 $CF_3CH_2OH$ (≈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 $\mu$mol) 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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## References

1 See, for example, R. Filler, *Isr. J. Chem.*, *17* (1978) 71; M. Zupan, *Vestn. Slov. Kem. Drus.*, *31* (1984) 151.
2 See, for example, R. W. Cockman and E. A. V. Ebsworth, *J. Chem. Soc., Chem. Commun.*, (1988) 529; E. A. V. Ebsworth, J. H. Holloway, N. J. Pilkington and D. W. H. Rankin, *Angew. Chem., Int. Ed. Engl.*, *23* (1984) 630.
3 M. J. Shaw, H. H. Hyman and R. Filler, *J. Org. Chem.*, *36* (1971) 2917; M. Ya. Turkina and I. P. Grageror, *J. Org. Chem., USSR*, *11* (1975) 335.
4 K. O. Christe and W. W. Wilson, *J. Fluorine Chem.*, *47* (1990) 117.
5 J. H. Holloway, *J. Chem. Soc., Chem. Commun.*, (1966) 22.
6 M. R. Colsman, T. D. Newbound, L. J. Marshall, M. D. Noirot, M. M. Miller, G. P. Wulfsberg, J. S. Frye, O. P. Anderson and S. H. Strauss, *J. Am. Chem. Soc.*, *112* (1990) 2349.
7 W. W. Dukat, J. H. Holloway, E. G. Hope, M. R. Rieland, P. J. Townson and R. L. Powell, *Eur. Pat. 92 301 531.7* (1992); paper in preparation.
8 J. H. Holloway, E. G. Hope, P. J. Townson and R. L. Powell, *Eur. Pat. 92 301 532.5* (1992); paper in preparation.
9 L. A. Buggey and E. G. Hope, unpublished work.