

^{19}F NMR and UV studies of xenon difluoride solution-vessel stability and its relevance to the fluorination of organic substrates

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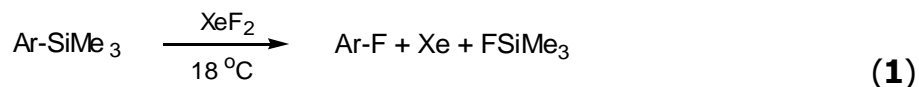
Abstract

The stability of xenon difluoride in CH_2Cl_2 , CHCl_3 , CFCl_3 , CH_3CN , H_2O and C_6F_6 , and the corresponding deuterated solvents, in PTFE-FEP, Pyrex[®] and quartz tubes has been investigated using ^{19}F NMR spectroscopy. Stability in tubes lined with PTFE-FEP is good. With the exception of CH_3CN , decomposition in Pyrex[®] tubes occurs within a few hours and this instability is attributable to coordination to Lewis acid sites on the glass surface. In quartz the lifetime of the xenon difluoride is extended by a few hours. The mode of reaction of xenon difluoride with organic substrates depends on the reaction vessel surface and the type of solvent. Pyrex[®] catalysis in a suitable solvent such as CH_2Cl_2 is a convenient way of achieving electrophilic reactions of xenon difluoride. The UV spectra of xenon difluoride in CH_3CN and $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (3:1) have been recorded.

Keywords: Xenon difluoride, stability, ^{19}F NMR, UV spectra, pyrex catalysis, fluorination

Introduction

Xenon difluoride is a stable, commercially available crystalline solid and potentially useful as a fluorinating agent in organic chemistry.^{1,2} In a series of studies we have shown that both solvent and reaction vessel can profoundly influence the mode of reaction of xenon difluoride with organic substrates.³⁻⁹ Although the instability of xenon difluoride in glassware has been known for some time, Pyrex[®] flasks have been widely used, and advocated,² for carrying out organic reactions but, apart from our own work,⁵ the role of the glass surface in determining the reaction pathway has not been recognised. We have shown, for example, that aryltrimethylsilanes are rapidly fluorinated by xenon difluoride at room temperature (Equation 1) but only in a Pyrex[®] flask.^{3,9}



This reaction is not observed in a quartz or FEP (fluorinated ethylene propylene) flask or in a Pyrex[®] flask previously washed with alkali.^{5,9} We interpret these observations in terms of a mechanism in which the borosilicate surface acts as a Lewis acid (or possibly a Brønsted acid) catalyst to which the xenon difluoride forms a dative bond ($\text{FXeF} + \text{A} \rightarrow \text{FXe}^{\delta+} \cdots \text{F} \rightarrow \text{A}^{\delta-}$). The polarised xenon difluoride may then react *via* an electrophilic mechanism in which the electrophile can be formally regarded as an $[\text{FXe}^+]$ equivalent. This proposal is consistent with borosilicate glass, such as Pyrex[®], containing 13% B_2O_3 and 2% Al_2O_3 .

Even in a Pyrex[®] flask the reactions shown in Equation 1, and other reactions, are completely inhibited if the solvent is acetonitrile. Since nitriles are weak Lewis bases, we believe that this solvent occupies all the acidic sites on the glass surface and prevents catalysis. Under these conditions, or in quartz or FEP flasks, xenon difluoride remains covalent/unpolarised and appears to react *via* a single electron transfer (SET) mechanism ($\text{M} + \text{XeF}_2 \rightarrow \text{M}^{+\cdot} + \text{XeF}_2^{\cdot-} \rightarrow \text{XeF}^{\cdot} + \text{F}^{\cdot}$)^{5,10} to give products *via* radical intermediates. These mechanistic conclusions are supported by our studies of reactions of other substrates in which the product composition is determined by the combination of solvent and vessel. These include studies of TMS benzoates,⁴ enol ethers⁶ and carboxylic acids.⁸

With the intention of supporting our preparative and mechanistic studies by identifying the species present in solution under organic reaction conditions, we have determined the ¹⁹F NMR and UV spectra of xenon difluoride in various solvent/cell systems. In this paper we report the results and demonstrate their relevance to (i) interpreting reaction mechanisms of xenon difluoride with organic substrates and (ii) choice of suitable reaction conditions. An examination of the literature reveals that this type of spectroscopic analysis in organic solvents is limited. The choice of NMR solvents for inorganic studies of xenon species has been briefly discussed.¹¹ We have previously reported an NMR study of the decomposition of XeF_2 in chloroform under various conditions,⁷ and results for this solvent are not included here except for direct comparison with those for dichloromethane.

Results and Discussion

¹⁹F NMR Spectroscopy

Several groups have previously studied aspects of the ¹⁹F NMR spectrum of XeF_2 using the following systems: aqueous HF/Teflon¹² or Kel-F,¹³ MeCN/glass,¹⁴⁻¹⁶ SO_2ClF /glass,¹¹ BrF_5 /glass,¹¹ HF/FEP,¹¹ hydrohalogenocarbons/FEP¹⁷ and solid XeF_2 /quartz.¹⁸ However, the influence of vessel surface on stability and decomposition over time has not previously been studied and discussed. We have studied XeF_2 stability in four discrete solvent groups: (a) CH_2Cl_2 , CHCl_3 and CFCl_3 ; (b) CH_3CN and CD_3CN ; (c) H_2O , D_2O and $\text{D}_2\text{O}/\text{CD}_3\text{CN}$; (d) C_6F_6 . For each group we have studied stability in (i) Pyrex[®] tubes containing a PTFE-FEP liner and (ii)

Pyrex[®] and quartz tubes (including tubes pre-washed with alkali (aq. NaOH)). The ¹⁹F NMR spectrum of unionised XeF₂ is characterised by both a singlet and a doublet. The latter arises from coupling of fluorine with the isotope ¹²⁹Xe (J_{F-Xe} ca. 5600 Hz), which occurs in 26.4% natural abundance, and the ¹⁹F signal therefore appears as a pseudo-triplet ($\delta = ca -175$).

(a) CH₂Cl₂, CHCl₃ and CFCl₃

(i) PTFE-FEP. Under PTFE-FEP/CH₂Cl₂ conditions almost no decomposition of XeF₂ has occurred after twenty-four hours and decomposition only begins to be detectable after two days. The sample is still >75% unionised XeF₂ after one week. The main products [CH₂FCI ($\delta -172.9$); CHFCl₂($\delta -84.0$); CF₂Cl₂ ($\delta +62.1$); HF ($\delta -193.3$)] are those reported by Holloway and co-workers under similar conditions,¹⁷ although we consistently observe greater amounts of CF₂Cl₂. At all times the amount of CHFCl₂ (H-F exchange) is small and exceeded by the amount of CF₂Cl₂, indicating the ease of H-F exchange in CHFCl₂. Under these conditions XeF₂ is more stable in CH₂Cl₂ than in CHCl₃ probably because the H-CCl₃ bond is more reactive (*cf* H-CFCI₂ above) towards XeF₂ than the H-CHCl₂ bond. For this reason CH₂Cl₂ is a more suitable solvent for XeF₂ reactions in plastic vessels. In PTFE-FEP/CFCI₃ there is no detectable decomposition of XeF₂ after one week and no evidence of CF₂Cl₂ formation. For this reason CFCI₃ is an excellent solvent for XeF₂ reactions, especially if solvent derived by-products need to be avoided. However, for environmental reasons this solvent is increasingly difficult to obtain.

(ii) Pyrex[®] and quartz. In Pyrex[®]/CH₂Cl₂ the ¹⁹F spectrum of XeF₂ is unchanged after ten minutes but most has decomposed after one hour and decomposition is complete after two hours. The products are CHFCl₂ ($\delta -81$), CH₂FCI ($\delta -170$) and fluoride [$\delta -149$ (broad), -157 (sharp) and -162 (sharp)]. When the tube was emptied and refilled with pure solvent the broad signal at $\delta -149$ remained suggesting that it is due to fluoride bound to the Pyrex[®] surface. Sometimes this signal resolves into two signals ($\delta -148.5$ and -149.1) suggesting two discrete binding sites. The signals at $\delta -157$ and $\delta -162$ are attributable to F⁻ and HF₂⁻ in solution. The lifetime of XeF₂ was considerably extended in quartz/CH₂Cl₂ with no decomposition after two hours, after which decomposition to fluoride [$\delta -128$ (bound) and -162 (unbound)], together with smaller amounts of CHFCl₂ and CH₂FCI, begins and is complete after about four hours. Significantly the bound fluoride in quartz is observed at a different position to that in Pyrex[®] ($\delta -128$ vs $\delta -149$) and is a sharp signal suggesting only one binding site. In both Pyrex[®] and quartz a pre-wash of the tube with 2N NaOH extends the lifetime of XeF₂ in CH₂Cl₂ by approximately one hour. These results are very similar to those obtained for CHCl₃ and CDCl₃ under the same conditions,⁷ except that CHCl₃ appears to be more reactive and therefore less suitable as a solvent. Similar stabilities in Pyrex[®] and quartz were obtained using CFCI₃ as solvent except that only fluoride (bound and unbound) was detected as decomposition product and, as for PTFE-FEP reactions, this solvent is superior to CH₂Cl₂ and CHCl₃.

Clearly the stability profiles of XeF₂ in Pyrex[®]/CH₂Cl₂, CHCl₃ and CFCI₃ are quite different to those in PTFE-FEP. We observed no ¹⁹F NMR evidence of surface bound XeF₂ and most of

the XeF₂ must be in solution. These results are consistent with XeF₂ bonding to Lewis acid sites on the glass surface and the bound reagent (FXe^{δ+}---F→Pyrex^{δ-}) either rapidly reacting as an electrophile (≡XeF⁺) with solvent (or substrate) or, alternatively, being reduced to fluoride (bound or unbound)(XeF₂ + 2e⁻ → Xe + 2F⁻). The latter reaction limits the lifetime of the XeF₂ and for reactions in glass necessitates the use of more than one equivalent. These surface interactions do not occur in PTFE-FEP.

(b) CH₃CN and CD₃CN

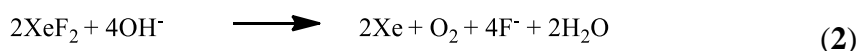
(i) PTFE-FEP. Under PTFE-FEP/CD₃CN conditions no decomposition of XeF₂ had occurred after one week.

(ii) Pyrex[®] and quartz. In Pyrex[®]/CD₃CN the XeF₂ is stable for several hours with a small amount of decomposition having occurred after twenty-four hours giving DF (δ -186.2; t, J 70 Hz) and HF (δ -183.5; d, J 485 Hz). The protons in the HF are presumably derived from the Pyrex[®] surface. Only the HF signal was observed in Pyrex[®]/CH₃CN. After three days all the XeF₂ had decomposed giving fluoride [δ -151.8 (bound) and -165.8 (unbound)] as the only detectable product. Greater stability was observed in quartz in which little decomposition to fluoride had occurred after five days. If either the Pyrex[®] or the quartz tubes were pre-washed with alkali the stability was further increased with no detectable decomposition after ten days. In Pyrex[®] and quartz XeF₂ is clearly much more stable in CH₃CN solution than in the chlorocarbon solvents. This observation is consistent with our suggestion that acetonitrile acts as a base and blocks the acidic catalytic sites on the glass surface.

(c) H₂O, D₂O and D₂O/CD₃CN

(i) PTFE-FEP. Some difficulty was encountered in running spectra in H₂O or D₂O using a PTFE-FEP liner due to the narrow bore of the liner and the viscosity of the solvent, which resulted in gas pockets in the sample. Spectra obtained using PTFE-FEP/D₂O showed that the sample was more than half decomposed after one hour, mainly fluoride after seven hours, and completely decomposed after twenty-four hours.

(ii) Pyrex[®] and quartz. In Pyrex[®]/H₂O no decomposition had occurred after thirty minutes but little XeF₂ remained after three hours and all had decomposed after seven hours to give bound and unbound fluoride. The same results were obtained using D₂O. In alkali washed Pyrex[®] decomposition was much more rapid with decomposition complete within thirty minutes giving fluoride (bound) as the only product. XeF₂ is known to undergo alkaline hydrolysis (Equation 2)^{12,19} and in contrast to other solvents the alkali wash catalyses the decomposition of XeF₂ in water. Similar results were obtained in quartz and alkali washed quartz.



In the absence of alkali XeF₂ is more stable in aqueous solution than might be expected. Satisfactory spectra for covalent XeF₂ were obtained in 3:1 CD₃CN: D₂O in Pyrex[®]. A mild reaction was observed in the alkali washed Pyrex[®] but this was much slower than in pure D₂O.

(d) C₆F₆

PTFE-FEP and Pyrex[®]. Although the ¹⁹F NMR resonance of XeF₂ (δ -182.8) is close to that of C₆F₆ (δ -166.6), the XeF₂ is easily detected in C₆F₆ solution. In the PTFE-FEP liner XeF₂ was less soluble in C₆F₆ than in other solvents and the solid only partially dissolved (50 mg added to 0.5 mL). Even after seven days some solid XeF₂ remained but the NMR signal was still strong and there was no evidence of decomposition products.

In a Pyrex[®] tube XeF₂ was detected after twenty minutes. After three hours the solution had turned yellow and there was effervescence due to xenon formation. Xenon difluoride was still detectable after four hours but after twenty-four hours all the XeF₂ had gone and the solution was pale brown, together with formation of a black/brown insoluble residue. No decomposition products were detected in the ¹⁹F NMR spectrum of the solution.

Table 1. Approximate half-lives (*t*_{0.5}) and lifetimes (*t*_{1.0}) of XeF₂ in vessel/solvent systems

Solvent	PTFE-FEP		Pyrex		Quartz	
	<i>t</i> _{0.5}	<i>t</i> _{1.0}	<i>t</i> _{0.5}	<i>t</i> _{1.0}	<i>t</i> _{0.5}	<i>t</i> _{1.0}
CH ₂ Cl ₂	>168 h	»168 h	0.6 h	2 h	2.5	4
					h	h
CHCl ₃	100 h	150 h	0.25 h	0.6 h	2.5	4
					h	h
CFCl ₃	>168 h	»168 h	1 h	2.5 h	1.5	3
					h	h
	>168 h	»168 h	48 h	72 h	>168 h	»168 h
CH ₃ CN						
H ₂ O	<1 h	<24 h	2 h	7 h	1.5	4
					h	h
C ₆ F ₆	>168 h	»168 h	4 h	10 h	-	-

UV Spectroscopy

Reports of the UV spectrum of xenon difluoride are very limited and, as far as we are aware, have only been described for the gas phase²⁰ and aqueous solution.²¹ Gaseous XeF₂ shows a weak absorbance at λ_{\max} 230 nm and in water the corresponding absorption is at λ_{\max} 242 nm. For studies of the formation of [¹⁸F]-XeF₂,^{22,23} UV spectroscopy proved to be a valuable tool for identifying and monitoring XeF₂ during chromatographic purification of [¹⁸F] exchanged product. It therefore became important to have UV data on various solvent systems including 3:1 acetonitrile: water. Because the λ_{\max} value for XeF₂ is below 250 nm, studies were necessarily limited to the use of quartz cells which operate across the whole UV range to as low as 190 nm.

Glass and polythene operate down to 350 nm and polymethylmethacrylate (Perspex) operates to 275 nm at lowest. Spectra were not determined in chloroform solution as its transmission at the wavelengths required (*ca.* 250 nm) is only 20%. We also avoided the use of pure water in the quartz cells. Although our NMR studies suggest that XeF₂ does not interact with quartz on a relatively short timescale (30 min), we wished to avoid damage to the cuvette surface.

Initial measurements on 1.5×10^{-2} M solutions using pure solvent as reference gave spectra with λ_{max} 245 nm in pure acetonitrile solution and λ_{max} 244 nm in 3:1 acetonitrile: water. To firmly establish that this absorption is due to XeF₂, and is not associated with the solvent, the spectrum in acetonitrile was determined at two other concentrations. The constancy of the extinction coefficient (ϵ) upon halving the concentration [26.9 mM, λ_{max} 245 nm (ϵ 58); 13.5 mM, λ_{max} 245 nm (ϵ 53)] confirmed that the species responsible is XeF₂. These results enable XeF₂ to be positively identified and assayed during elution using MeCN or MeCN: H₂O mixtures.^{22,23}

Conclusions

The stability of XeF₂ under different reaction conditions is summarized in Table 1, which shows the approximate time for half ($t_{0.5}$) and complete ($t_{1.0}$) decomposition. In plastic vessels CH₂Cl₂, CFC₃, CH₃CN and C₆F₆ are all suitable solvents. Water and CHCl₃ are less appropriate because of their reactivity towards XeF₂. Pyrex[®] or quartz flasks can be used as alternatives to plastic vessels if CH₃CN is used as solvent, particularly if the flask is pre-washed with alkali. For reactions in which catalysis by the Pyrex[®] surface is desirable all the halogenated solvents have suitable profiles. Dichloromethane is the preferred solvent since it is less reactive than chloroform, more environmentally acceptable than CFC₃ and easier to remove than C₆F₆. Surprisingly, the lifetime of XeF₂ in Pyrex[®]/H₂O appears to be longer than in the halogenated solvents, probably because the water, like acetonitrile, can act as a weak Lewis base. Although we have used dried solvents stored over activated molecular sieve for our studies, the use of 'wet' CH₂Cl₂ in limited trials did not seem to adversely affect the course of reactions.

Provided reactions are reasonably fast, Pyrex[®]/CH₂Cl₂ is a good medium for carrying out electrophilic reactions of XeF₂. The Pyrex[®] appears to activate the reagent (FXe^{δ+}---F→Pyrex^{δ-}) but reduction to fluoride (XeF₂ + 2e⁻ → Xe + 2F⁻) simultaneously occurs necessitating the use of more than one equivalent of XeF₂. The use of a Pyrex[®] flask as a heterogeneous catalyst may have advantages as well as the usual conveniences of a solid-supported reagent. For fluorodesilylation of 1-trimethylsilyl-4-fluorobenzene (Equation 1: Ar = 4-FC₆H₄) the use of a homogeneous catalyst (BF₃.OEt₂ in FEP/CH₂Cl₂) is reported to give a completely different product profile²⁴ to the Pyrex[®]-catalysed reactions.⁹

Experimental Section

General. ^{19}F NMR spectra were recorded on a Bruker Advance DPX300 NMR spectrometer operating at 282 MHz and using trichlorofluoromethane as an external standard. Standard Pyrex[®] glass thin walled (5mm) NMR tubes were used and 8 inch PTFE-FEP NMR tube liners (Wilma 6005) and quartz NMR tubes (Wilma 507-PP-QTZ) were purchased from Fluorochem Ltd. NMR solutions were prepared using *ca* 50 mg of XeF_2 in 0.5 mL solvent. Tubes were washed with chromic acid and rinsed with distilled water and then acetone prior to drying in an oven overnight at 80 °C. Alkali washed NMR tubes were prepared by rinsing acid washed tubes with water followed by 2N NaOH and then rinsing with acetone prior to drying. The acquisition time for ^{19}F NMR spectra was 44 seconds and, after recording the starting spectrum, spectra were run at 0.5, 1, 2, 4, 8, 24, 36, 48 and, when appropriate, 96, 168 and 300 hour intervals. UV spectra were determined on a Varian CARY 1C UV-Visible spectrophotometer using quartz cuvettes. Solutions were initially prepared in a glove box atmosphere of dry nitrogen by dissolving XeF_2 (200 mg) in the desired solvent (4 mL). Xenon difluoride was purchased from Apollo Scientific Ltd.

Supplementary Material

The supplementary material contains the ^{19}F NMR spectra of XeF_2 in Pyrex[®]/ CH_2Cl_2 after 10 and 100 minutes, and the UV spectrum of XeF_2 in 3:1 acetonitrile: water.

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References

1. Filler, R. *Israel J. Chem.* **1978**, *17*, 71.
2. Tius, M. A. *Tetrahedron* **1995**, *51*, 6605.
3. Lothian, A. P.; Ramsden, C. A. *Synlett* **1993**, 753.
4. Nongkunsarn, P.; Ramsden, C. A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 121.
5. Ramsden, C. A.; Smith, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6842.
6. Ramsden, C. A.; Smith, R. G. *Org. Lett.* **1999**, *1*, 1591.
7. Shaw, M. M.; Smith, R. G.; Ramsden, C. A. *J. Fluorine Chem.* **2002**, *11*, 671.
8. Ramsden, C. A.; Shaw, M. M. *Tet. Lett.* **2009**, *50*, 3321.
9. Lothian, A. P.; Ramsden, C. A.; Shaw, M. M.; Smith, R. G. *Tetrahedron* **2011**, *67*, 2788.

10. Bardin, V. V.; Stennikova, I. V.; Furin, G. G.; Leshina, T. V.; Yakobson, G.G. *J. Gen. Chem. USSR* **1988**, *58*, 2297-2303.
11. Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard C. *Inorg. Chem.* **1978**, *17*, 980.
12. *Noble-Gas Compounds*, Hyman, H. H., Ed.; University of Chicago Press: Chicago, 1963.
13. Gillespie, R. J.; Netzer, A.; Schrobilgen G. J. *Inorg. Chem.* **1974**, *13*, 1455.
14. Meinert, H.; Rüdiger, S. *Z. Chem.* **1967**, *7*, 239.
15. Ingman, L. P.; Jokisaari, J.; Oikarinen, K.; Seydoux R. *J. Magn. Reson., Series A* **1994**, *111*, 155.
16. Lounila, J.; Oikarinen, K.; Ingman, P.; Jokisaari, J. *J. Magn. Reson., Series A* **1996**, *118*, 50.
17. Dukat, W. W.; Holloway, J. H.; Hope, E. G.; Townson, P. J.; Powell, R. L. *J. Fluorine Chem.* **1993**, *62*, 293.
18. Hindermann, D. K.; Falconer, W. E. *J. Chem. Phys.* **1969**, *50*, 1203.
19. Appleman, E. H. *Inorg. Chem.* **1967**, *6*, 1268.
20. Pysh, E. S.; Jortner, J.; Rice, S. A. *J. Chem. Phys.* **1964**, *40*, 2018.
21. Appleman, E. H.; Malm, J. G. *J. Am. Chem. Soc.* **1964**, *86*, 2297.
22. Constantinou, M.; Aigbirhio, F. I.; Smith, R. G.; Ramsden, C. A.; Pike, V. W. *J. Am. Chem. Soc.* **2001**, *123*, 1780.
23. Lu, S.; Pike, V. W. *J. Fluorine Chem.* **2010**, *131*, 1032.
24. Bardin, V. V.; Frohn, H. J. *J. Fluorine Chem.* **1998**, *90*, 93.