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Theoretical Evidence for Two New Intermediate Xenon Species: Xenon Azide Fluoride, $FXe(N_3)$, and Xenon Isocyanate Fluoride, FXe(NCO)[†]

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The reaction behavior of xenon difluoride, XeF_2, toward HN_3, NaN_3, and NaOCN was investigated in H_2O, aHF (anhydrous HF), and SO_2ClF solution. The analysis of the final reaction products ($XeF_2 + HN_3$ (NaN_3) in $H_2O \rightarrow$ HF, N_2, N_2O, Xe; $XeF_2 + HN_3$ in aHF $\rightarrow N_2$, Xe, N_2F_2; XeF_2 + HOCN (NaOCN) in $H_2O \rightarrow$ HF, N_2, N_2O, NH_3, CO_2, Xe) indicated the intermediate formation of $FXe(N_3)$ and FXe(NCO) and revealed different reaction mechanisms for both compounds. Both intermediates, $FXe(N_3)$ and FXe(NCO), were studied on the basis of ab initio computations at HF and correlated MP2 levels using a quasirelativistic LANL2DZ pseudopotential for Xe. Both were shown to possess stable minima at HF and MP2 levels (no imaginary frequencies) with the following structural parameters (MP2/LANL2DZ). $FXe(N_3)$: C_s; $d(\text{F}-\text{Xe}) = 2.051$, $d(\text{Xe}-\text{N1}) = 2.318$, $d(\text{N1}-\text{N2}) = 1.241$, $d(\text{N2}-\text{N3}) = 1.180$ Å; $\angle(\text{FXeN1}) = 178.1$, $\angle(\text{XeN1N2}) = 112.2$, $\angle(\text{N1N2N3}) = 174.7°$. FXe(NCO): C_s; $d(\text{F}-\text{Xe}) = 2.024$, $d(\text{Xe}-\text{N}) = 2.206$, $d(\text{N}-\text{C}) = 1.194$, $d(\text{C}-\text{N}) = 1.231$ Å; $\angle(\text{FXeN}) = 178.7$, $\angle(\text{XeNC}) = 125.4$, $\angle(\text{NCO}) = 174.2°$. The experimentally unobserved cyanate isomer, FXe(OCN), was calculated to be higher in energy than the isocyanate isomer FXe(NCO): $\Delta E = 19.8$ (HF), 18.3 (MP2) kcal mol^{-1}.

Introduction

We have been studying various neutral compounds and cations containing a direct main-group-element-azide bond.[1] Due to the lability of the nitrogen−iodine bond (all binary N−I species and more than a few compounds containing a direct N−I bond are very unstable and often explosive), we especially focused on iodine azide compounds, *e.g.* IN_3, $(IN_3)_x$, $I(N_3)_2^+$, and $I_2N_3^+$.[2] This pronounced instability of many N−I compounds has facilitated both experimental and theoretical research exploring the thermodynamics of such compounds and especially the N−I bond energy.[3,4]

We now want to explore xenon azide compounds since Xe is the next neighbor of iodine. (*N.B.* Although XeF^+ is a well-known and stable cation, the isoelectronic counterpart to I_2, XeI^+, is still an unknown species.) For an excellent review covering the history of xenon chemistry see ref 5.

Whereas numerous examples of xenon bonded to oxygen or fluorine are known, much fewer compounds containing a direct Xe−N bond have been reported. The first Xe−N compound $FXeN(SO_2F)_2$ was prepared by DesMarteau et al. in 1974,[6] and it was not before 1987 that Schrobilgen et al. reported the XeF^+ cation bonded to H−CN, *i.e.* $[HC{\equiv}N{-}Xe{-}F]^+$.[7] Further xenon−nitrogen-bonded derivatives of the $-N(SO_2F)_2$ and $-N(SO_2CF_3)_2$ groups[8] as well as XeF^+ cations bonded to other organo−nitrogen ligands have been reported.[9]

Experimental Section

Caution**!** Neat hydrazoic acid is shock sensitive, and proper safety precautions, such as working on a small scale and using safety shields, should be taken when the material is handled.

Materials. XeF_2 (Fluorochem), NaN_3 (Aldrich), and NaOCN (Aldrich) were used as supplied. HF (Merck) was dried by storage over BiF_5.[10] HN_3 was prepared from NaN_3 and stearic acid at 110−130 °C.[11]

Apparatus. All reactions were carried out on a vacuum line constructed largely from 316 stainless steel and nickel to which the reaction vessel was connected via ≈1 ft length, $^1/_4$ in. o.d. flexible FEP tubing. The T-shaped reaction vessel originally described by Bartlett et al. was constructed from FEP tubing (Bohlender). The commonly

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Table 1. Gaseous Products of the Reactions of XeF_2 with HN_3/NaN_3 and XeF_2 with NaOCN

reaction	solvent	IR/cm^{-1}	assignment	ref
$HN_3 + XeF_2$	aHF	990^a	ν_5, ν_{as}(N−F), *trans*-N_2F_2	21
$HN_3 + XeF_2$	H_2O	3338 vw^b	ν(N−H), HN_3	3
		2565 w	2 × ν_3, N_2O	22
		2298 vw	2 × ν_s(NNN), HN_3	3
		2225 s	ν_1(NN), N_2O	22
		2140 m	ν_{as}(NNN), HN_3	3
		2075 vw	δ (NNN), HN_3	3
		1285 m	ν_3(NO), N_2O	22
		1151 w	ν_s(NNN), HN_3	3
		590 w	ν_2(δ, NNO), N_2O	22
$NaN_3 + XeF_2$	H_2O	2225 s	ν_1(NN), N_2O	22
		2140 m	ν_{as}(NNN), HN_3	3
		2075 vw	δ (NNN), HN_3	3
		1285 m	ν_3(NO), N_2O	22
		1151 w	ν_s(NNN), HN_3	3
		590 w	ν_2(δ, NNO), N_2O	22
NaOCN + XeF_2	H_2O	3718 m	CO_2[23]	23
		3618 m	CO_2[23]	23
		2568 w	2 × ν_3, N_2O	22
		2355 vs	ν_3(ν,OCO), CO_2	23
		2228 s	ν_1(NN), N_2O	22
		1282 m	ν_3(NO), N_2O	22
		720 m	CO_2[23]	23
		665 s	ν_2(δ, OCO), CO_2	23

[a] Beside HF, NH_3, and small amounts of HN_3. [b] Beside HF.

used reactor was constructed from 3/4 in. o.d. FEP tubes which were joined at right angles by a Teflon valve (Bohlender).[12]

Spectroscopy. Gas infrared spectra were recorded at 20 °C (2 mmHg, 10 cm Monel cell, NaCl windows) on a Philips PU9800 FTIR spectrometer. The NMR spectra (^{14}N, ^{19}F) were recorded in 10 mm NMR tubes using a Bruker WP 200 SY spectrometer operating at 14.462 MHz (^{14}N) or 188.313 MHz, respectively. NMR spectra in aHF solution were recorded in 8 mm FEP NMR tubes fitted into 10 mm glass NMR tubes. All spectra are reported in ppm on the δ scale and are referred to external $MeNO_2$ (^{14}N) or $CFCl_3$ (^{19}F), respectively. Good ^{14}N spectra could usually be obtained after 5000 scans and a pulse width of 48 μs, and ^{19}F spectra, after 20 scans and a pulse width of 2 μs. Peak positions appearing downfield (high frequency) of the reference are reported as *plus* and those upfield (low frequency) of the reference are reported as *minus*.

We also attempted to observe ^{129}Xe NMR spectra (55.316 MHz; directly referenced to external $XeOF_4$); however, the only resonance found could be assigned to XeF_2 ($\delta = -1680$ ppm, triplet, $^2J_{Xe-F}$(^{129}Xe satellites) = 5604 Hz.).[9c]

Computational Methods. The structures and the vibrational spectra of the molecules $FXe(N_3)$, FXe(NCO), and FXe(OCN) were computed ab initio at the HF and electron-correlated MP2 levels of theory with the program package Gaussian 94.[13] For C, N, O, and F, a 6-31G(d) basis set was used; for Xe, a quasi-relativistic pseudopotential (LANL2DZ)[14] was used where the basis functions for the valence s and p electrons consist of the standard double-ζ basis set (notation HF/LANL2DZ or MP2/LANL2DZ). An NBO analysis was carried out to account for non-Lewis contributions to the most appropriate valence structure. In the quantum mechanical computation (NBO analysis, subjecting the HF density matrix as represented in the localized NBOs to a second-order perturbative analysis), the energy for the donor−acceptor interaction was computed according to eq 1 with h^F being the Fock operator.[15]

$$E^{(2)}_{\varphi\varphi^*} = -2\frac{\langle\varphi|\mathbf{h}^{\mathbf{F}}|\varphi^*\rangle^2}{E\varphi^* - E\varphi} \qquad (1)$$

Reaction of HN_3 with XeF_2 in aHF. In a typical reaction, XeF_2 (0.51 g, 3.01 mmol) was dissolved in aHF (5 mL) in one arm of an FEP T-reactor and HN_3 (0.13 g, 3.02 mmol) was dissolved in aHF (5 mL) in the other arm. Both solutions were cooled to −78°C. The HN_3 solution was slowly added to the XeF_2 solution. When the addition was complete, the colorless solution was allowed to slowly warm to room temperature. No reaction was observed at or below −20 °C. At ca. −18 °C, the fast reaction started with evolution of gaseous products. Cessation of the gas evolution signaled completion of the reaction. The gaseous products were analyzed by gas IR spectroscopy (Table 1).

Reaction of HN_3 with XeF_2 in H_2O. This reaction was carried out as described above for the reaction of XeF_2 with HN_3 in aHF with the difference that both solutions were reacted at 0 °C (HN_3, 0.13 g, 3.02 mmol; in 3 mL of H_2O/XeF_2, 0.51 g, 3.01 mmol; in 7 mL of H_2O). A pinkish color appeared for a short moment. The total volume of the gaseous products formed corresponded to 7.0 mmol of gas (calculated from expansion of the reaction products from the known-volume reaction vessel into the calibrated vacuum line). Variation of the temperature at which the reaction vessel was held revealed ca. 3.4 mmol of N_2, 1.1 mmol of N_2O, and 2.5 mmol of Xe (bp: N_2, −196 °C; N_2O, −88.5 °C; Xe, −108.1 °C).[11b] The gaseous products were analyzed by gas IR spectroscopy (Table 1). The mass spectrum of the gaseous products which were volatile at −196 °C revealed the presence of a large amount of N_2 (and traces of O_2, the level of which was close to that of the "background" air).

Reaction of NaN_3 with XeF_2 in H_2O. This reaction was carried out as described above for the reaction of XeF_2 with HN_3 in H_2O at 0 °C (NaN_3, 0.20 g, 3.08 mmol/XeF_2, 0.51 g, 3.01 mmol). The gaseous products were analyzed by gas IR spectroscopy (Table 1).

NMR Experiment: Reaction of HN_3 with XeF_2 in aHF. In an NMR experiment, XeF_2 (0.38 g, 2.24 mmol) was reacted with HN_3 (0.01 g, 2.24 mmol) in 5 mL of aHF. Below −20 °C, HN_3 (^{14}N NMR) and XeF_2 (^{19}F NMR) were detected. During the rapid reaction, no spectrum could be obtained due to bubbling of the solution. Immediately after cessation of the gas evolution, the sample was recooled to −40 °C and N_2F_2 was detected in the ^{14}N NMR spectrum.

Before reaction: ^{14}N NMR (−30 °C, aHF) −134 (N2, HN_3), −162 (N3, HN_3), −318 ppm (N1, HN_3);[16] ^{19}F NMR (−30 °C, aHF) −175 ppm (XeF_2), $^2J_{Xe-F}$(^{129}Xe satellites) = 5611 Hz.[17]

After reaction: ^{14}N NMR (−40 °C, aHF) +67 ppm, t, $^1J_{N-F}$ = 137 Hz (*trans*-N_2F_2);[18a] ^{19}F NMR (−40 °C, aHF) +95 ppm s, br (*trans*-N_2F_2).[18a]

NMR Experiment: Reaction of HN_3 with XeF_2 in SO_2ClF. The NMR experiment in SO_2ClF was performed with the same amounts of XeF_2 and HN_3 as described above for the NMR experiment in aHF. Before the reaction started, only HN_3 and XeF_2 were detected in the ^{14}N and ^{19}F NMR spectra. After the reaction started ($T_{max} = -20$ °C), however, before it was complete, the NMR tube was rapidly recooled to −80 °C. The spectra obtained at this temperature were indicative for a mixture of the starting materials (XeF_2 and HN_3) and the final products; however, no intermediate was detected. N_2F_2 could not be detected in the ^{19}F NMR spectrum of the quenched-reaction mixture due to the strong solvent resonance of SO_2ClF at +100 ppm.

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Before reaction: ^{14}N NMR (−30 °C, SO_2ClF) −136 (N2, HN_3), −169 (N3, HN_3), −324 ppm (N1, HN_3);[16] ^{19}F NMR (−30 °C, SO_2ClF) −174.8 ppm (XeF_2), $^{2}J_{Xe-F}$(^{129}Xe satellites) = 5605 Hz.[17]

Recooled during reaction: ^{14}N NMR (−80 °C, SO_2ClF) +63 ppm, s, br (*trans*-N_2F_2),[18a] −136 (N2, HN_3), −172 (N3, HN_3), −324 ppm (N1, HN_3);[16] ^{19}F NMR (−80 °C, SO_2ClF) −175.0 ppm (XeF_2), $^{2}J_{Xe-F}$(^{129}Xe satellites) = 5606 Hz.[17]

Reaction of NaOCN with XeF_2 in H_2O. In a typical reaction, XeF_2 (0.51 g, 3.01 mmol) was dissolved in H_2O (6 mL) in one arm of an FEP T-reactor and NaOCN (0.20 g; 3.08 mmol) was dissolved in H_2O (6 mL) in the other arm. Both solutions were cooled to 0 °C. The NaOCN solution was slowly added to the XeF_2 solution. The fast reaction started immediately with evolution of gaseous products. A pinkish color appeared for a short moment. Cessation of the gas evolution signaled completion of the reaction. The gaseous products were analyzed by gas IR spectroscopy (Table 1). Ammonia was detected by its characteristic odor and identified as [$Hg_2NI·H_2O$].[18b]

NMR Experiment: Reaction of NaOCN with XeF_2 in aHF. In an NMR experiment, XeF_2 (0.38 g, 2.24 mmol) was reacted with NaOCN (0.15 g, 2.31 mmol) in 5 mL of aHF. Below −20 °C, HNCO (formed from NaOCN in aHF; ^{14}N NMR) and XeF_2 (^{19}F NMR) were detected. During the rapid reaction, no spectrum could be obtained due to bubbling of the solution. Immediately after cessation of the gas evolution, the sample was recooled to −40 °C.

Before reaction: ^{14}N NMR (−30 °C, aHF) −304 ppm (H*N*CO);[19] ^{19}F NMR (−30 °C, aHF) −175.1 ppm (XeF_2), $^{2}J_{Xe-F}$(^{129}Xe satellites) = 5611 Hz.[17]

After reaction: no ^{14}N NMR (−40 °C, aHF) resonance found.

NMR Experiment: Reaction of NaOCN with XeF_2 in H_2O. This reaction was carried out as described above for the reaction of XeF_2 with NaOCN in aHF with the difference that both solutions were reacted at 0 °C (NaOCN, 0.15 g, 2.31 mmol/XeF_2, 0.38 g, 2.24 mmol). Immediately after cessation of the gas evolution, the NMR spectrum was recorded at 0 °C and NH_4^+ was detected in the ^{14}N NMR spectrum.

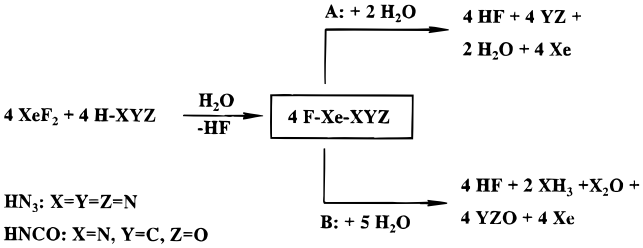
After reaction: ^{14}N NMR (0 °C, aHF) −355.0 ppm (NH_4^+).[20]

Due to the very poor solubility of NaOCN in SO_2ClF, no attempt was made to obtain NMR data in this solvent.

Results and Discussion

Reactions in Water. It is well-known that fluorine gas reacts at room temperature with moist NaN_3 or with NaN_3 suspended in H_2O/HF to intermediately form N_3F, which thermally decomposes into N_2 and NF radicals, which then combine to give N_2F_2.[24] However, in no experiment in which we reacted NaN_3, HN_3, or NaOCN with XeF_2 in aqueous conditions did we observe the formation of N_2F_2 (see below for reaction of NaN_3 in aHF). Although we cannot completely rule out that any N_2F_2 formed in the course of the reaction could have entirely hydrolyzed by the time the reaction was over, it is far less likely that XeF_2 behaves as a simple fluorination agent in these reactions but intermediately forms F−Xe−N_3 or F−Xe−NCO, respectively (*cf.* Scheme 1). Both intermediates (F−Xe−N_3 and F−Xe−NCO) are not expected to be stable in water but are expected to hydrolyze according to mechanism A or B shown in Scheme 1.

Scheme 1. Pathways for the Formation and Decomposition of $FXeN_3$ and FXe(NCO)



Whereas N_2O was identified by IR spectroscopy (Table 1) as one of the products of the azide as well as of the isocyanate reaction in water, NH_3 was only detected as a reaction product in the reaction of NaOCN with XeF_2 (^{14}N NMR, NH_4^+ in solution; analytically in H_2O solution, Experimental Section). Moreover, the volumetric analysis of the gaseous products formed in the reaction of HN_3 with XeF_2 in water revealed that for *4* equiv of reacted XeF_2 (or HN_3; *cf.* Scheme 1 and Experimental Section) and 9.4 equiv of gaseous products were found (N_2, 4.5; N_2O, ca. 1.5; Xe, ca. 3.4 equiv). This corresponds within experimental errors to mechanism A (Scheme 1), where one would expect the total formation of 10 equiv of gas (*i.e.*: N_2, 4.0; N_2O, 2.0; Xe, 4.0 equiv), rather than to mechanism B (total 9 equiv: N_2, 0.0; N_2O, 5.0; Xe, 4.0 equiv). (*N.B.* The volumetric analysis for the products of the isocyanate reaction was not conclusive due to the high solubility of ammonia and carbon dioxide in water.) The brief observation of the pinkish color (see Experimental Section) for both the cyanate and the azide reactions with XeF_2 in aqueous solution indicates a short-lived derivative of the aqueous system only. So far, we have been unable to identify this species; it could, for example, be a short-lived product of the interaction of HON (formed from HON_3 or HONCO) with water.

Both mechanisms (A and B) can easily be understood by initial hydrolysis of the Xe−F and Xe−N bonds according to their polarity (eqs 2 and 3). It is known that thermal fragmentation of covalently bound azides, XN_3, is induced not by breaking the X−N_3 bond but rather by dissociation into XN and N_2 (*i.e.*, HN_3 decomposes into HN and N_2).[3,25] Therefore, HON_3 will dissociate into N_2 and HON radicals which will combine into hyponitrous acid, *i.e. trans*-$(HNO)_2$ (eq 4).[26] Although neat hyponitrous acid is known,[27 a] the compound rapidly decomposes to form N_2O and H_2O (eq 5).[27b] In case of mechanism B (isocyanate reaction), the initially formed H−O−NCO (eq 3) reacts with water according to eq 6 to form (i) carbonic acid, which liberates CO_2 (eq 7), and (ii) hydroxylamine, which decomposes into a complex mixture of NH_3, N_2O, and H_2O

$$\mathrm{F{-}Xe{-}N_3 + H_2O \rightarrow H{-}O{-}N_3 + HF + Xe} \qquad (2)$$

$$\mathrm{F{-}Xe{-}NCO + H_2O \rightarrow H{-}O{-}NCO + HF + Xe} \qquad (3)$$

$$\mathrm{HON_3 \rightarrow \{HON\} + N_2 \rightarrow {}^{1}/_{2}\ \mathit{trans}\text{-}HO{-}N{=}N{-}OH + N_2} \qquad (4)$$

$$\mathrm{\mathit{trans}\text{-}HO{-}N{=}N{-}OH \rightarrow N_2O + H_2O} \qquad (5)$$

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Table 2. Ab Initio Calculated Energies and Structural Parameters of $FXeN_3$, FXeNCO, and FXe(OCN) (Notation: F−Xe−A−B−C)

	$FXeN_3$		FXeNCO		FXe(OCN)	
	HF[a]	MP2[a]	HF[a]	MP2[a]	HF[a]	MP2[a]
$-E$/a.u.	277.681 89	278.415 03	281.608 47	282.286 74	281.576 83	282.257 64
d(F−Xe)/Å	1.980	2.051	1.944	2.024	1.910	2.009
d(Xe−A)/Å	2.184	2.318	2.138	2.206	2.139	2.207
d(A-B)/Å	1.218	1.241	1.192	1.194	1.265	1.292
d(B-C)/Å	1.107	1.180	1.158	1.231	1.142	1.192
∠(FXeA)/deg	178.2	178.1	178.9	178.7	178.5	179.1
∠(XeAB)/deg	114.6	112.2	134.5	125.4	119.2	113.7
∠(ABC)/deg	177.2	174.7	177.4	174.2	178.8	179.1

[a] For C, N, O, and F, a 6-31G(d) basis set was used; for Xe, a quasi-relativistic pseudopotential (LANL2DZ)[14] was used where the basis functions for the valence s and p electrons consist of the standard double-ζ basis set (notation: HF/LANL2DZ or MP2/LANL2DZ).

Table 3. Ab Initio Calculated Frequencies (cm^{-1}), Intensities in Parentheses (km mol^{-1}), and Zero-Point Energies (zpe) of $FXeN_3$, FXeNCO, and FXe(OCN) (Notation: F−Xe−A−B−C)

	$FXeN_3$		FXeNCO		FXe(OCN)	
approx assign	HF[a]	MP2[a]	HF[a]	MP2[a]	HF[a]	MP2[a]
ν_{as}(ABC), A′	2425 (1245)	2246 (836)	2439 (2521)	2300 (1147)	2572 (464)	2194 (140)
ν_{s}(ABC), A′	1375 (492)	1251 (24)	1519 (49)	1325 (25)	1256 (248)	1325 (25)
δ(ABC), A′	759 (10)	645 (1)	756 (62)	637 (14)	697 (44)	586 (24)
γ(ABC), A″	694 (27)	551 (6)	713 (73)	580 (24)	622 (32)	497 (10)
ν(FXe), A′	511 (411)	470 (92)	562 (261)	482 (165)	608 (212)	482 (138)
ν(XeABC), A′	403 (57)	277 (1)	385 (152)	344 (16)	402 (108)	350 (0)
δ(FXeABC),A′	243 (28)	186 (15)	233 (48)	199 (29)	228 (25)	187 (18)
γ(FXeABC),A″	221 (38)	172 (21)	240 (41)	200 (30)	236 (32)	200 (15)
δ(FXeABC), A′	118 (8)	95 (5)	82 (5)	86 (29)	108 (12)	98 (9)
zpe/kcal mol^{-1}	9.65	8.44	9.91	8.80	9.62	8.16

[a] For C, N, O, and F, a 6-31G(d) basis set was used; for Xe, a quasi-relativistic pseudopotential (LANL2DZ)[14] was used where the basis functions for the valence s and p electrons consist of the standard double-ζ basis set (notation: HF/LANL2DZ or MP2/LANL2DZ).

(eq 8) (occasionally, some N_2 is formed as well during the decomposition of hydroxylamine).[27c]

$$H{-}O{-}NCO + 2H_2O \rightarrow HONH_2 + (HO)_2CO \qquad (6)$$

$$(HO)_2CO \rightarrow H_2O + CO_2 \qquad (7)$$

$$HONH_2 \rightarrow {}^1/_4N_2O + {}^3/_4H_2O + {}^1/_2NH_3 \qquad (8)$$

Reactions in aHF. Whereas we do have evidence for the intermediate formation of $FXeN_3$ and FXe(NCO) in water, the final products from the reactions carried out in aHF are in accord with both (i) the intermediate formation of $FXeN_3$ and FXe(NCO) and (ii) the behavior of XeF_2 as a fluorinating agent, yielding FN_3 and or FNCO, respectively, and HF (NaF). We unequivocally identified small amounts of *trans*-N_2F_2 from the IR and $^{14}N/^{19}F$ NMR spectra looking at the products formed from the reaction of HN_3 and XeF_2 in aHF (eq 9).

$$FN_3 \xrightarrow{aHF} \{FN\} + N_2 \rightarrow {}^1/_2\ trans\text{-}N_2F_2 + N_2 \qquad (9)$$

Thermodynamic Aspects. The formation of $FXeN_3$ and FXe(NCO) from XeF_2 and HN_3 or HNCO is thermodynamically feasible (largely due to the strong H−F bond) as indicated by an energy cycle describing the gas phase reactions according to eqs 10 and 11. The *upper* (*i.e.*, in reality, more negative)

$$XeF_2(g) + HN_3(g) \rightarrow FXeN_3(g) + HF(g) \qquad (10)$$

$$XeF_2(g) + HNCO(g) \rightarrow FXeNCO(g) + HF(g) \qquad (11)$$

values for $\Delta H°$ could be estimated using the literature data for the bond enthalpies and taking the Xe−N bond dissociation enthalpy equal to zero:[28] $\Delta H°(10) < -12.1$ kcal mol^{-1}; $\Delta H°(11) < -12.1$ kcal mol^{-1}.

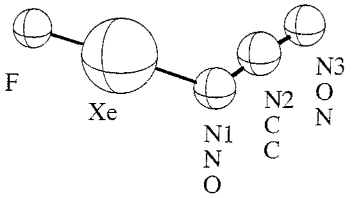

Figure 1. Structures of $FXeN_3$, FXeNCO, and FXe(OCN).

Computational Aspects. The structures of both observed intermediates, $FXeN_3$ and FXe(NCO), as well as the structure of the cyanate isomer, FXe(OCN), were computed ab initio at the HF and electron-correlated MP2 levels of theory and were fully optimized within C_s symmetry (Table 2, Figure 1). For xenon, a quasi-relativistic pseudopotential was used. All three molecules represent true minima at the energy hypersurface (no imaginary frequencies; Table 3). The experimentally *un*observed cyanate isomer FXe(OCN) (*N.B.* Neither H_2O_2 nor HOCN—the most likely products of the decomposition of the hypothetical FXe(OCN), *i.e.* of HO−OCN—was detected) was found to be 19.8 kcal mol^{-1} (HF level) and 18.3 kcal mol^{-1} (MP2 level) higher in energy than the isocyanate form FXe(NCO) (Table 2). This finding nicely compares to the fact that O=C−N−N−C=O is also much lower in energy than the O−O bound isomer N≡C−O−O−C≡N (*e.g.*, isocyanate radicals, $O{=}C{=}N^\bullet$, are much more stable than cyanate radicals $N{\equiv}C{-}O^\bullet$).[29,30]

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(28) (a) Bond enthalpy terms at 298.15 K (all values in kcal mol^{-1}): Xe−F (XeF_2), 31.3;[11b] H−N (HN_3), 92.2;[28b] H−F (HF), 135.6.[11b] (b) Illenberger, E.; Comita, P. B.; Brauman, J. I.; Fenzlaff, H.-P.; Heni, M.; Heinrich, N.; Koch, W.; Frenking, G. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1026.

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The MP2-computed F−Xe bond lengths for $FXeN_3$ and FXe(NCO) of 2.05 and 2.02 Å are just slightly longer than the experimentally determined value of 1.97 Å for the F−Xe bond in the covalent molecule $FXeN(SO_2F)_2$, which also contains divalent xenon directly bound to one fluorine and one nitrogen atom (*cf.* XeF_2, d(Xe−F) = 1.977 Å).[6,8,9c] Whereas the Xe−N bond length of 2.20 Å in $FXeN(SO_2F)_2$[6,8] compares well to the calculated value of 2.21 Å in FXe(NCO), the Xe−N bond in the azide was computed to be 2.32 Å and is therefore expected to be substantially weaker than that in the iminodisulfuryl derivative. On the other hand, the Xe−N bond length in $FXeN_3$ is still substantially shorter than the calculated Xe−N bond length in the cationic adduct $[FXe(NCH)]^+$ (2.42 Å).[9c] The relatively weak Xe−N bond in $FXeN_3$ can be rationalized in the localized picture by an NBO analysis. A strong donor−acceptor interaction (negative hyperconjugation) which weakens the Xe−N bond was found for $FXeN_3$: $\sigma(\text{Xe}-\text{N1}) \rightarrow \pi^*(\text{N2}-\text{N3})$, 52 kcal mol^{-1}. (*N.B.* This interaction is much stronger in $FXeN_3$ than in FXe(NCO).)

Conclusions

The reaction behavior of XeF_2 toward azides and isocyanates has been studied experimentally in aqueous solution and in aHF. From the experimental and theoretical results discussed in this paper, the following conclusions can de drawn: (i) The formation of the observed hydrolysis products in the reaction of XeF_2 with HN_3 (or NaN_3) and HNCO (or NaOCN) in water can mechanistically be better explained by an intermediate formation of $FXe(N_3)$ and FXe(NCO) than by a simple fluorination of the azide and isocyanate. No experimental evidence was found for the formation of the isomeric cyanate compound FXe(OCN). (ii) Xenon azide fluoride, $FXe(N_3)$, and xenon isocyanate fluoride, FXe(NCO), both possess minimum structures (true minima; no imaginary frequencies) on their energy hypersurface at HF and electron-correlated MP2 levels of theory. (iii) The isomeric cyanate compound FXe(OCN) also represents true minima at HF and MP2 levels; however, this isomer is higher in energy than the isocyanate species by 19.8 kcal mol^{-1} (HF level) and 18.3 kcal mol^{-1} (MP2 level).

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