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A Charge-Transfer Complex of Xenon and Difluorovinylidene

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Since the pioneering work of Bartlett et al.¹ a number of xenon compounds with electronegative elements (halogen, O, N) have been reported in the literature, while compounds with bonds to other elements, in particular carbon, are still rare. In 1979, Lagow et al.² claimed the synthesis of Xe(CF₃)₂; however, the unequivocal spectroscopic characterization of this compound is still lacking. Frohn et al.³ described the X-ray structure of [C₆F₅Xe]⁺, a stable, crystalline cation with a Xe–C bond distance of 2.092 Å. Recently Räsänen et al. reported on the matrix isolation of the linear HXeH molecule,⁴ a neutral molecule which does not contain electronegative elements, and several HXeX (X = Cl, CN, etc.) molecules.⁵ The bonding of these molecules may be described as resonance hybrid between A–Xe⁺–B[–] and A[–]–Xe⁺–B with a positively charged xenon atom. Since the bonding of charge-transfer compounds of type A–Xe–A and A–Xe–B is essentially due to Coulombic attraction, the stability of these species depends on the electron affinity (EA) of fragments A and B, respectively.

The interaction of electron deficient singlet ground-state carbenes R₂C: and Xe could similarly lead to an attractive charge-transfer interaction and formation of compounds of type R₂C[–]–Xe⁺. A carbene that is ideally suited to study the interactions with Xe is difluorovinylidene (**1**). The EA of **1** in the gas phase was determined by Lineberger et al. using negative ion photoelectron spectroscopy to 2.255 eV, almost five times higher than that of the parent vinylidene H₂C=C:.^{6,7} In contrast, the EA of difluorocarbene F₂C: is only 0.170 eV.⁸ We recently demonstrated that high yields of **1** are obtained by irradiation (λ = 193 nm) of matrix-isolated (argon, 10 K) difluoroacetylene (**2**).⁹ Vinylidene **1** is stable under the conditions of matrix isolation, but rapidly reacts with CO or N₂ even at cryogenic temperatures (Scheme 1).

The photochemistry of acetylene **2** and thermal reactions of vinylidene **1** were investigated in Ar, Xe, 0.5% Xe-doped Ar and 0.5% Kr-doped Ar matrices. Irradiation of **2** in Ar at 7 K with an ArF excimer laser (λ = 193 nm) produces **1** and **2** in a

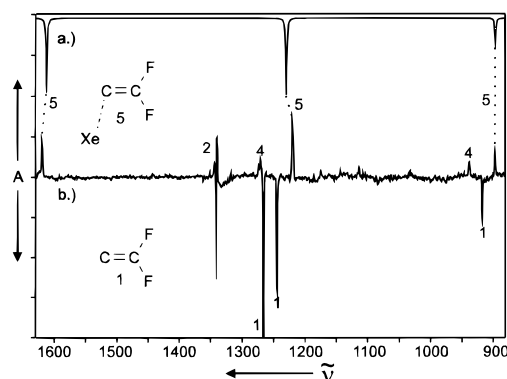
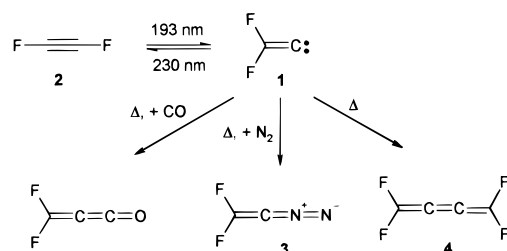


Figure 1. (a) Calculated spectrum of **5** (MP2/RCEP, TZ2Pf) scaled by 0.979. (b) IR difference spectrum showing the annealing of **1** in a 0.5% Xe-doped Ar matrix: bottom, bands disappearing; top, bands appearing on annealing at 40 K.

Scheme 1



photostationary equilibrium with up to 90% of **1**. Irradiation with a high-pressure mercury lamp (λ > 230 nm) of a mixture of **1** and **2** recovers acetylene **2** nearly quantitatively. Interestingly, 193 nm irradiation of **2** in Xe does not lead to any photoproduct, while irradiation in solid Ar capped with Xe produces the same mixture of **1** and **2** as without Xe-capping. This clearly demonstrates that the lack of photoreactivity of **2** in Xe does not result from a filtering effect of Xe.

Annealing of **1** in Ar at temperatures higher than 25 K enables the diffusion of N₂, which is always present in the matrix as a contamination from small leaks in the vacuum system. Due to the high mobility of N₂ and its reactivity toward **1**, diazo compound **3** is rapidly formed. Temperatures higher than 35 K enable the diffusion of vinylidene **1** and formation of further thermal products. The main product with IR absorptions at 1735, 1271, and 938 cm^{–1} was identified as tetrafluorobutatriene (**4**) by comparison with the gas-phase IR spectrum¹⁰ and ab initio calculations (Scheme 1).¹¹ Other IR bands of thermal products of **1** could not yet be assigned.

Irradiation of **2** in Ar doped with 0.5% Xe at 7 K produces the same mixture of **1** and **2** as irradiation in pure Ar. Annealing at 40 K, however, yields **3**, **4**, and a novel set of IR absorptions at 1620, 1220, and 898 cm^{–1} (Figure 1, Table 1). Obviously, carbene **1** is trapped by Xe and a new compound **5** is formed. (Under the same conditions, no reaction between **1** and krypton takes place.) Irradiation of **5** with 193 nm does not produce **1**, but rather leads back to acetylene **2**. This could explain why neither **1** nor **5** is observed in a neat Xe matrix. The vinylidene **1** formed during the photolysis of **2** immediately reacts with Xe

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(11) MP2/6-311G(d) scaled by 0.97: 1740 (b_{1u}, C=C=C str.), 1281 (b_{2u}, asym F–C–F str), 938 (b_{1u}, sym F–C–F str) cm^{–1}. Further vibrational bands (77, 114, 142, 192, 348, 395, 515, 520, 532, 569, 616, 677, 1272, 1367, 2174) have no significant IR intensities.

Table 1. Computed^a Harmonic and Experimental Vibrational Wavenumbers (cm⁻¹) of F₂CC*Xe (**5**)

mode (sym)	description	basis set			expt ^e	shift	
		I ^b	II ^c	III ^d		calcd ^f	expt ^g
1 (a')	CC str + CF ₂ str (in phase)	1651	1640	1647 (211)	1620 (50)	-65	-52
2	CF ₂ str (out of phase)	1259	1243	1255 (218)	1220 (100)	-50	-47
3	CF ₂ str (in phase) + CC str	916	908	915 (76)	898 (40)	-27	-20
4	CF ₂ scissors + CF ₂ rock + XeCC def	566	568	572 (4)			
5	mainly CF ₂ scissors (+ CF ₂ rock)	517	518	522 (31)		+1	
6	XeCC def + CXe str + CF ₂ rock	188	202	196 (21)			
7	CXe str + XeCC def	120	136	129 (7)			
8 (a'')	CF ₂ out of plane	577	573	579 (3)		-7	
9	XeCCF(cis) torsion	167	173	172 (4)			

^a At the MP2 level of theory using the frozen core approximation. ^b MP2/RCEP,TZ2Pf. ^c MP2/RCEP,aug-cc-pVTZ. ^d MP2/AE,TZ2Pf, IR band intensities (km/mol) in parentheses. ^e In Ar at 10 K, rel intensities (based on the strongest absorption) in parentheses. ^f Calcd (MP2/RCEP,TZ2Pf) shifts relative to **1**. ^g Shifts relative to **1** in argon at 10 K.

Table 2. Computed^a Equilibrium Geometries (Å, deg) of F₂CC*Xe (**5**) and F₂CC (**1**)

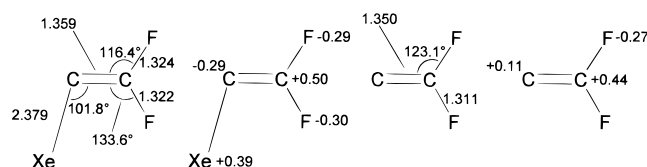
param ^b	F ₂ CC*Xe basis set			F ₂ CC basis set	
	I	II	III	I, III ^c	II
CC	1.359	1.359	1.358	1.350	1.351
CF cis	1.322	1.326	1.324	1.311	1.313
CF trans	1.324	1.327	1.325	1.311	1.313
CCF cis	133.6	133.8	133.8	123.1	123.1
CCF trans	116.4	116.6	116.4	123.1	123.1
CXe	2.379	2.335	2.350		
XeCC	101.8	101.7	102.0		

^a At the MP2 level of theory using the frozen core approximation. ^b The labels "cis" and "trans" refer only to F₂CC*Xe (**5**). ^c Basis sets I and III are identical for the isolated F₂CC molecule (**1**).

to give **5**, which is photolyzed back to acetylene **2** and Xe. Thus, Xe acts as a photocatalyst for the **1** → **2** transformation, similar to N₂.⁹

Compared to the CC stretching vibration (1672 cm⁻¹), the asymmetrical (1267 cm⁻¹), and the symmetrical (918 cm⁻¹) CF₂ stretching vibrations of **1**, the IR absorptions of **5** are red-shifted by 52, 47, and 20 cm⁻¹, respectively.

To assign the IR spectrum and to investigate the electronic structure of the adduct of **1** and Xe, ab initio calculations were performed at the MP2(fc) level using three large basis sets (I–III).^{12,13} Relativistic effects for Xe are implicitly included in basis I and II which employ relativistic effective core potentials for Xe.¹⁷ The theoretical results for the vibrational wavenumbers (Table 1) and the equilibrium geometries (Table 2) are quite similar for basis sets I–III; hence, relativistic effects are apparently not dominant for these properties. For the sake of brevity, the following discussion will always refer to the MP2/I data (unless noted otherwise). A minimum **5** is found on the F₂C₂Xe potential surface with an uncorrected binding energy of 3.6 kcal/mol relative to F₂CC + Xe (2.8 kcal/mol with counterpoise corrections, 2.0 kcal/mol with additional zero-point corrections). The Xe atom is positioned in the F₂CC plane, the CCXe bond angle calculated

Scheme 2

to 102°, and the distance between the terminal carbon atom and Xe to 2.38 Å (Scheme 2, Table 2). Since the CXe potential is flat, the uncertainty in the calculated CXe distance is expected to be large. Compared to that of **1**, the CC distance as well as the CF bond distances in **5** are elongated by ca. 0.01 Å. This corresponds to the observed red-shifts of the CC and CF stretching vibrations. Due to a repulsive interaction of the Xe atom with one of the fluorine atoms, the CCF bond angle for the cis fluorine atom is considerably larger (133.6°) than that for the trans fluorine atom (116.4°).

The calculated IR spectrum of **5** (from harmonic wavenumbers scaled by 0.979, which gives the best fit of the calculated and experimental spectrum of **1**) nicely reproduces the experimental spectrum (Figure 1, Table 1). It is quite surprising that despite the low binding energy of the Xe atom the three observed IR absorptions are red-shifted up to 52 cm⁻¹.

The bonding in **5** is described best as a charge-transfer complex with the Xe atom donating electron density to the in-plane vacant p-orbital of the vinylidene. In **1** as well as in **5** the F₂C group carries only a very small negative charge (-0.11 and -0.10 e, respectively, natural population analysis (NPA) charges are used throughout this discussion). However, while in **1** the terminal C atom is slightly positive (+0.11 e), in **5** this C atom is negatively charged (-0.29 e) and the Xe atom carries a positive charge of +0.39 e. Consequently, with 3.18 D, the dipole moment of **5** is much larger than that of **1** (1.09 D).

The computed binding energy of **5** depends on the theoretical method employed. At the Hartree-Fock level, the potential surface for F₂CC + Xe is repulsive. At the correlated MP2 level, the uncorrected binding energies are 3.6, 6.1, and 3.9 kcal/mol for basis sets I–III, respectively. These values are slightly reduced by counterpoise and zero-point corrections (see above) so that the best MP2 estimate is around 3 kcal/mol. Exploratory optimizations at the coupled-cluster level (CCSD(T)/I) indicate a larger Xe–C distance and a smaller binding energy (compared with MP2/I) but confirm that **5** is bound relative to F₂CC + Xe.

In summary, **1** is the singlet carbene with the highest reactivity observed so far. It not only dimerizes or reacts with CO and N₂ at cryogenic temperatures, but also forms with Xe a charge-transfer complex revealing a distinct IR spectrum.

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(12) Abbreviations: MP2(fc) Møller–Plesset second-order perturbation theory with frozen cores; aug-cc-pVTZ augmented polarized valence triple- ζ basis;^{14,15} TZ2Pf triple- ζ basis¹⁶ with cc-pVTZ polarization functions;¹⁴ RCEP relativistic compact effective potentials and associated valence basis set;¹⁷ AE all-electron basis.

(13) Basis I: TZ2Pf for C and F, RCEP for Xe with a (5s5p)/[3s3p] contraction and additional polarization functions (exponents: d 0.25, 0.36; f 0.40). Basis II: aug-cc-pVTZ for C and F, Xe as in basis I with additional diffuse s, p, and d functions (exponents: s and p 0.03247, d 0.13). Basis III: TZ2Pf for C and F, AE basis for Xe¹⁸ with a (24s19p14d)/[16s14p8d] contraction and additional f functions (exponents: 0.503940, 2.8625).

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