Oxidation of Difluorovinylidene

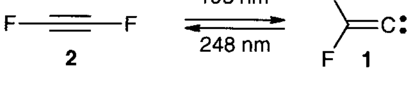
Carsten Kötting, Wolfram Sander,* Michael Senzlober, and Hans Bürger

Abstract: Difluorovinylidene is a highly reactive and extremely electrophilic singlet carbene that thermally abstracts an oxygen atom from CO_2 at temperatures as low as 30 K. The resulting difluoroketene is characterized for the first time using IR spectroscopy in combination with isotopic labeling and density functional theory (DFT) calculations. The three observed IR absorptions of the ketene at 1274, 1427, and 2162 cm^{-1} are assigned to the asymmetrical FCF stretching vibration and the asymmetrical and symmetrical CCO stretching vibrations, respectively. The oxidation of difluorovinylidene with $^3O_2$ results in a complex product mixture with CF_2, C_2F_4, CO_2, COF_2, and CO as the major products. A mechanism consistent with all observed products is proposed.

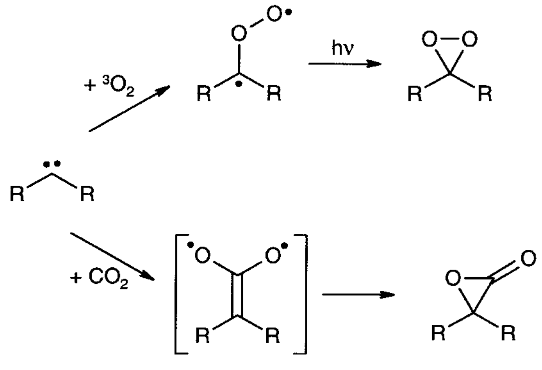
Keywords: carbenes · ketenes · matrix isolation · oxidations · vinylidenes

Introduction

Difluorovinylidene **1** is the first vinylidene that could be isolated and spectroscopically characterized in noble gas matrices.[1] Since **1** is obtained in a very clean and simple reaction by UV irradiation of matrix-isolated difluoroacetylene **2**, the reactivity with a variety of substrates can be investigated. The highly reactive vinylidene **1** not only adds CO and N_2 rapidly at temperatures as low as 20 K, [1] but also forms a weakly bound compound with xenon.[2] In this compound a substantial charge is transferred from Xe to the terminal carbon atom of **1**. This extreme electrophilicity of the singlet ground state carbene **1** is in line with its large electron affinity of 2.255 eV determined by negative-ion photoelectron spectroscopy in the gas phase.[29] Thus, **1** is the most electrophilic and most reactive carbene known to date and both the philicity and reactivity are in marked contrast to the stable nucleophilic singlet carbenes described by Arduengo et al.[30–32]



The reaction of $^3O_2$ with triplet[3–7] or singlet[8] carbenes leads to carbonyl *O*-oxides as the primary products.[9, 10] As expected, the spin-allowed reaction of triplet carbenes with $^3O_2$ is much faster than the reaction of singlet carbenes. Electron-withdrawing groups in the singlet carbenes increase the reaction rates of the electrophilic attack on $^3O_2$ (the reaction of most triplet carbenes is diffusion-controlled and independent of substituents). The carbonyl oxides are highly labile and on irradiation with visible light they eliminate oxygen atoms to give the corresponding carbonyl compounds or rearrange to give dioxiranes. This reaction sequence is now frequently used to identify carbenes isolated in matrices (Scheme 1).



Scheme 1. Mechanisms of the oxidation and carboxylation of carbenes.

In the solid state (matrix) the reaction of carbenes with CO_2 yields α-lactones (oxiranones) which could be matrix-isolated in several cases,[11–13] while in the gas phase fragmentation to CO and the corresponding carbonyl compounds predomi-

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nates.[14] A study of the influence of substituents on the reactivity of carbenes towards CO_2 suggests that the nucleophilicity rather than the spin state of the carbene governs its reactivity.[13] Thus, in contrast to the reactivity with $^3O_2$, electron-withdrawing groups decrease the reaction rates. From that it was concluded that the primary step is the nucleophilic attack of the carbene center to the CO_2 carbon atom to form a zwitterionic (or diradicaloid) intermediate, which subsequently ring-closes to give the α-lactone. It is therefore of interest to investigate the reaction of the extremely electrophilic **1** with both CO_2 and $^3O_2$.

Results and Discussion

Difluorovinylidene **1** is obtained in yields of up to 90% by irradiation ($\lambda = 193$ nm, ArF Excimer-Laser) of difluoroacetylene **2**, matrix-isolated in Ar at 7 K.[1] When **2** is irradiated in 0.5–1% O_2- or CO_2-doped Ar matrices, vinylidene **1** is still the major product, and only small amounts of new products are formed. Under these conditions most of the molecules of **1** are produced in matrix cages that do not contain the trapping reagents O_2 and CO_2, respectively, and thus no reaction occurs. On annealing doped argon matrices to 30–40 K, the diffusion of trapped species becomes rapid and the thermal formation of products can be directly monitored by IR spectroscopy.

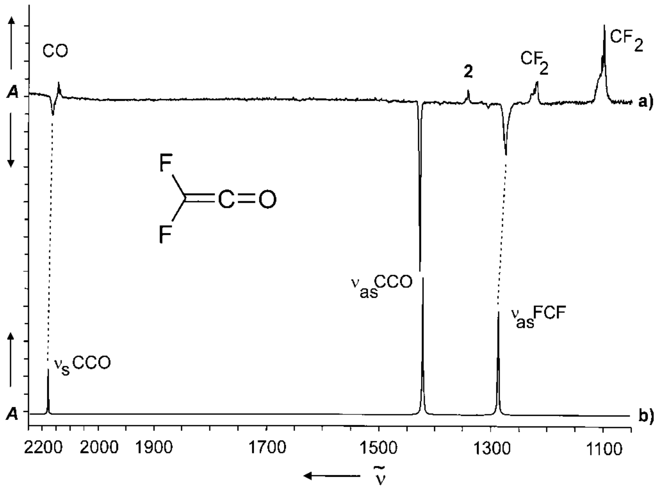
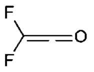
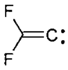
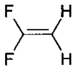
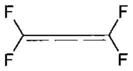
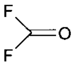
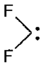
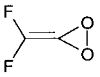


Figure 1. a) IR difference spectrum showing the photochemistry of difluoroketene **3** in argon at 7 K. Bottom part, bands disappearing; top part, bands appearing on irradiation with $\lambda > 550$ nm. b) Calculated spectrum of **3** (MP2/6–311G(d) scaled by 0.97).

Table 2. FCF stretching vibrations.

	ν_s (FCF)	ν_{as} (FCF)
	808[a,b]	1274
	918	1267
	919	1290
	938	1271
	967	1239
	1102	1221
	849/1304[a,c]	1301[a]

[a] Calculated (B3LYP/6–311G(d)). [b]$\nu_s(CF_2)$ mixes with ν(CC). [c]$\nu_s(CF_2)$ mixes with $\nu_s(CO_2)$.

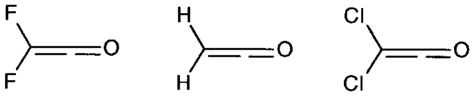
Annealing of **1** in a 1% CO_2-doped Ar matrix at 30 K results in the formation of CO (2138 cm^{-1}) and a new product **3** with IR absorptions at 1274, 1427, and 2162 cm^{-1} (Table 1, Figure 1). The vibration at 1274 cm^{-1} is characteristic of an asymmetrical FCF stretching vibration (Table 2), and the absorption at 2162 cm^{-1} of a heterocumulene C=C=X. To identify the newly formed compound **3** and to assign the observed vibrations, the experiment was repeated with both $^{13}CO_2$ and $C^{18}O_2$. With $^{13}CO_2$ none of the vibrations of **3** are shifted, and ^{13}CO (2091.4 cm^{-1}) is formed as the only CO isotopomer. This demonstrates that one of the oxygen atoms—but not the C atom—of CO_2 is transferred to **1**. Using $C^{18}O_2$ results in the formation of $C^{18}O$ (2087.5 cm^{-1}) and in significant red shifts of two of the absorptions of **3**: the band at 1427 cm^{-1} is red-shifted by 19 cm^{-1}, and the band at 2162 cm^{-1} by 22 cm^{-1}. These vibrations are assigned to the ν_s and ν_{as} CCO stretching vibration, respectively, of a ketene. The absorption at 1274 cm^{-1} is not affected by ^{18}O substitution, as expected for the ν_{asym} (FCF) stretching vibration orthogonal to the ν_{sym} and ν_{asym} (CCO) stretching modes. The IR spectra clearly reveal that the newly formed compound **3** is

Table 1. Experimental and calculated IR spectroscopic data of difluoroketene **3**.[a]

Entry	Sym	Ar, 10 K	$\Delta^{18}O$	MP2/6–311G(d) (scaled by 0.97)	$\Delta^{18}O$	B3LYP/6–311G(d)	$\Delta^{18}O$	Assignment
1	B_2	-		167.8 (0)	0	204.8 (2)	4	$\rho(CF2)_{(rock)}$
2	B_1	-		199.4 (2)	4	236.4 (0)	0	$\gamma(CF2)_{(wag)}$
3	B_1	-		374.6 (1)	5	380.8 (2)	5	$\gamma(COO)_{(oop)}$
4	A_1	-		450.4 (1)	4	456.4 (1)	4	$\delta(CF_2)$
5	B_2	-		660.1 (0)	1	682.0 (1)	2	δ(CCO)
6	A_1	-		785.5 (8)	11	808.1 (7)	11	$\nu_s(CF_2)$
7	B_2	1274.4 (80)	0	1286.1 (75)	0	1276.5 (70)	0	$\nu_{as}(CF_2)$
8	A_1	1426.8 (100)	19	1421.3 (100)	19	1463.6 (100)	20	ν_s(CCO)
9	A_1	2161.6 (42)	22	2180.1 (32)	22	2269.9 (59)	24	ν_{as}(CCO)

[a] Wavenumbers and ^{18}O shifts in cm^{-1}, relative intensities in parentheses.

the so far unknown difluoroketene. The frequency of ν_{as}(C-CO) is close to that of ketene **4** (in argon: 2142 cm^{-1})[26] and dichloroketene **5** (in argon: 2155 cm^{-1})[27], while ν_s(CCO) is blue-shifted by 46 cm^{-1} relative to **4** and 137 cm^{-1} relative to **5**.

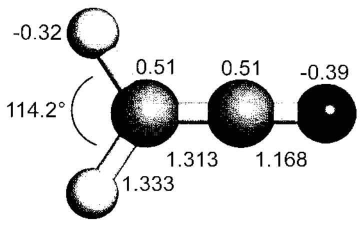


3 **4** **5**

This assignment is confirmed by MP2[17] and DFT[18, 19] calculations, which nicely reproduce band positions, intensities, and the isotopic shifts (Table 1, Figure 1). The ν_s (FCF) stretching vibration of **3** is calculated at 808 cm^{-1} (B3LYP), however, due to its low intensity it is not observed experimentally. The low intensity of this mode results from the small dipole moment of **3** and the mixing of the CF_2 vibration with the in-phase movement of the CO group. Other modes of **3** are predicted to be even lower in intensity.

Figure 2 shows some calculated properties of ketene **4** and difluoroketene **3**. The calculated geometry of **4** is very close to the geometry derived from microwave spectra, which demonstrates the reliability of the DFT calculations.[28] Bond lengths and NPA charges of the CCO group in **3** are similar to that in **4**, whereas the fluorine substitution results in a reduced XCX bond angle and a negative NPA charge of this carbon. Since the polarity of CF_2 is comparable to that of CO, the dipole moment decreases from 1.42 in **4** to 0.05 Debye in **3**.

a) Difluoroketene



b) Ketene

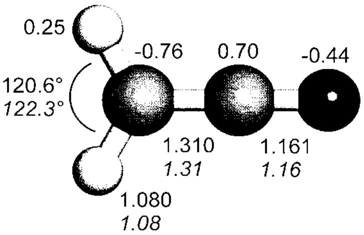
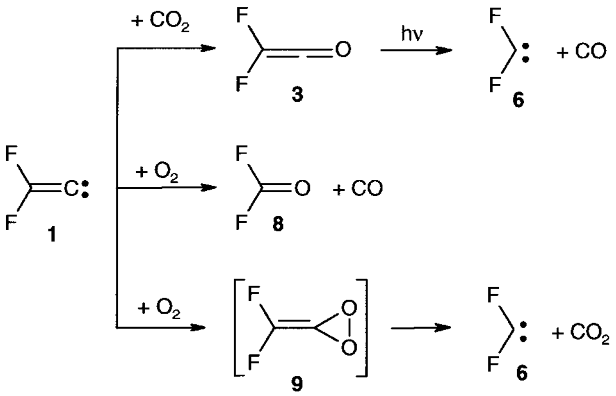


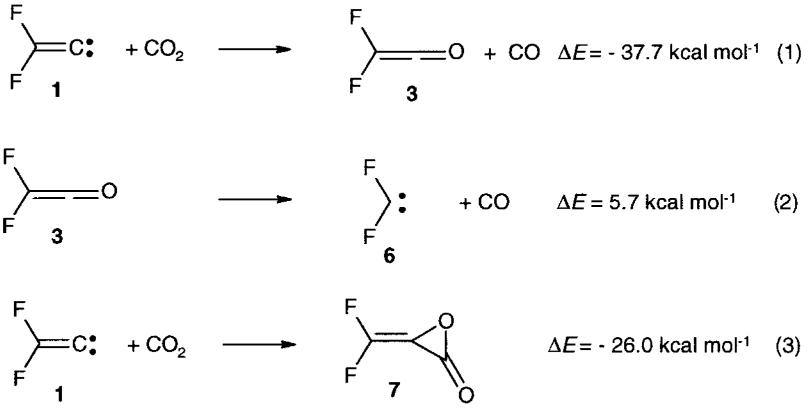
Figure 2. Geometry (bond angle in deg, bond lengths in Å) and NPA charges of a) difluoroketene **3** and b) ketene **4** calculated at the B3LYP/6–311(d,p) level of theory. The comparison of the calculated with experimental (in italics) geometry of **4** (ref. [28]) reveals the accuracy of the calculation.

Difluoroketene **3** is highly photolabile, and irradiation with visible light ($\lambda > 550$ nm) results in the complete fragmentation into CO and CF_2 (Figure 1, Scheme 2, Scheme 3). The reverse reaction is not observed: CF_2 can be matrix-isolated in neat CO, and neither annealing of the matrix nor UV or visible irradiation leads to **3**. Several attempts to synthesize **3** were reported in literature, however, in all cases only the products of the fragmentation were observed.[20–23] This suggests that the barrier of the fragmentation is small and that the equilibrium lies on the side of the fragments. This is in contrast to most other carbenes, which are rapidly trapped by CO even in CO-doped Ar matrices at 35–45 K.[10] Ab initio calculations by Boldyrev et al. predict that the fragmentation of **3** is almost thermoneutral, whereas the fragmentation of monofluoroketene and ketene **4** was calculated to be endothermic by 41.8 kcal mol^{-1} and 77.2 kcal mol^{-1} (experimental for **4**: 78 kcal mol^{-1}), respectively.[24]



Scheme 2. Reactions of difluorovinylidene **1** with CO_2 and O_2.

α-Lactones are stable under the conditions of matrix isolation,[11–13] and because in the reaction of **1** α-lactone **7** could not be observed—although the formation of **7** is estimated to be exothermic by 26 kcal mol^{-1}—we conclude that it is not formed. An alternative mechanism which accounts for the formation of **3** and CO and which does not involve **7** is the electrophilic attack of **1** on one of the oxygen atoms of CO_2. Thus, the oxygen abstraction results from the extreme electrophilicity of **1**.



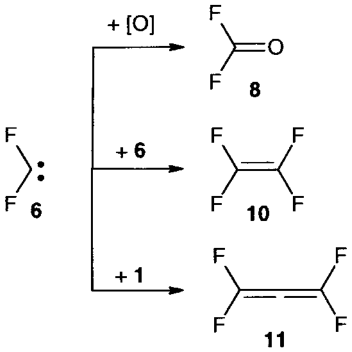
Scheme 3. Reaction energies calculated at the B3LYP/6-311G(d,p) + ZPE level of theory.

The photochemical and thermal reaction of vinylidene **1** in an 0.5 % O_2-doped argon matrix leads to a complex mixture of products (Table 3). During the irradiation of **2** in O_2-doped

Table 3. IR absorptions of the compounds observed in a 0.5 % O_2-doped Ar matrix containing vinylidene **1** after annealing at 35 K for several minutes.

Wavenumber	I_{rel}[a]	^{18}O shift[b]	Assignment
2345.4	100	35	CO_2
2163.1	5	24	**3**
2146.8	8	50	CO[c]
2138.4	12	50	CO (free)
2085.1	3		diazo[d]
2065.9	13		**11**
1941.2	19	32	**8**
1909.7	29	34	**8**
1860.7	7	41	?
1646.5	9		diazo[d]
1426.7	7	16	**3**
1340.9	79		**2**
1330.2	27		**10**
1295.9	6	6	**9**
1293.6	2	8	**9**
1274.4			**3**
1271.1	14		butatriene[e]
1266.7	6		**1**
1238.1	18		**11**
1179.0	40		**10**
1121.6	10		?
1115.8	7		?
1102.2	8		**6**
1067.2	6		?
1039.5	4	59	O_3
1034.7	14		**11**
969.9	5	15	**8**
764.7	8	5	**8**
660.7	11	8	CO_2

[a] Relative intensities of the IR absorption based on the CO_2 absorption. [b] Isotopic shifts if $^{18}O_2$ was used in the experiment. [c] CO complexed to other constitutents of the matrix. The structure of the complex is unknown. [d] Diazodifluoroethene formed by trapping of **1** with traces of N_2 in the matrix.[1] [e] Tetrafluorobutatriene formed by dimerization of **1**.[2]

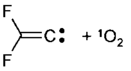
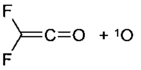
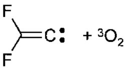
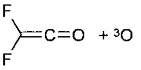
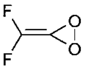
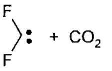
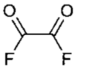
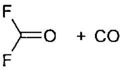


Scheme 4. Reactions of difluorocarbene **6**.

matrices ozone is formed, presumably by the reaction of oxygen atoms O(^3P) (formed by the 193 nm photolysis of O_2) with $^3O_2$. Major products of the oxidation of **1** are CO_2, CO, CF_2, and CF_2O (**8**). CF_2 rapidly dimerizes to give tetrafluoroethene **10** or is trapped by **1** to give tetrafluoroallene **11**, which are also observed in the matrix (Scheme 4). These products were also found in the thermal decomposition of acetylene **2**, which suggests that the **2**→**1** rearrangement occurs thermally at elevated temperatures.[25] Difluoroketene **3** is a minor product in the oxidation of **1**, presumably formed by a secondary reaction of **1** and CO_2 and not by the direct reaction with O_2 (Scheme 2).

The formation of CO_2 and CF_2 from **1** and O_2 requires an intermediate such as difluoromethylenedioxirane **9**. Several absorptions with very low intensity (e. g. at 1296 and 1294 cm^{-1}) are formed during the 193 nm irradiation of **2** in O_2-doped argon and disappear on warming the matrix to 35 K within several minutes. However, due to the low concentration in the matrix this intermediate could not be unambiguously identified. According to calculations at the B3LYP level of theory the formation of dioxirane **9** from **1** and $^3O_2$ is exothermic by 70.5 kcal mol^{-1}, and the decomposition of **9** to CF_2 and CO_2 releases another 96.7 kcal mol^{-1} (Table 4). Although the formation of dioxirane **9** as an intermediate in the oxidation of **1** is plausible, the direct spectroscopic characterization is still lacking.

Table 4. Relative energies (B3LYP/6-311G(d)) of some $C_2F_2O_2$ species.

	E_{rel} + ZPE
	235.1
	214.6
	196.1
	150.5
	125.6
	28.9
	0.7
	0.0

In summary, the reaction of vinylidene **1** with CO_2 leads to difluoroketene **3** and CO in high yields, while the reaction with molecular oxygen produces CF_2 and CO_2 as the principal products. Secondary thermal and photochemical reactions account for all minor products found in the matrix. The extreme reactivity of **1** is governed by its unprecedented electrophilicity.

Experimental Section

Matrix-isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Messer-Griesheim, 99.9999 %) on top of a CsI window with a rate of approximately 0.15 mmol min^{-1}. In order to prevent aggregation of difluoroacetylene **2**, depositions of the matrices were done at 7 K. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 0.5 cm^{-1} in the range of 400–4000 cm^{-1}.

The following gases were used for the doped matrices: O_2 (Messer Griesheim, 99.998 %), $^{18}O_2$ (Alfa, 99.51 atom % $^{18}O_2$), CO_2 (Messer Griesheim, 99.995 %), $C^{18}O_2$ (Alfa, 99.75 atom % $^{18}O_2$), $^{13}CO_2$(MSD-Isotopes, 99.3 atom % ^{13}C).

Irradiations were carried out with an ArF Excimer Laser ($\lambda = 193$ nm; Lambda Physik COMPex 100) or Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the mercury high-pressure arc lamp was absorbed by a 10 cm path of water. Schott cut off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Calculations were performed with the Gaussian94 program package.[15, 16] Frequency calculations were done at the B3LYP/6–311G(d,p)[18, 19] and the MP2/6–311G(d,p)[17] level of theory. Thermodynamic properties were calculated at the B3LYP/6–311G(d,p) level of theory and include the zero-point energy.

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