Matrix Isolation and ab Initio Molecular Orbital Study of Fluorocyclopropenone and Fluoro(ketenyl)carbene

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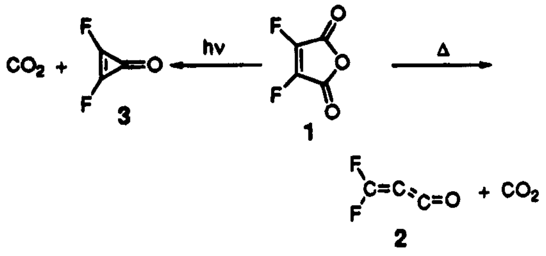
Received July 26, 1995®

Irradiation of fluoromaleic anhydride (**4**) under matrix isolation conditions in argon produces fluoro(ketenyl)carbene (**6s**) and fluorocyclopropenone (**7**) as primary photoproducts. Fluoro(ketenyl)carbene is quickly converted to fluoroacetylene and carbon monoxide under the irradiation conditions while fluorocyclopropenone is slowly converted to the same products. The photochemical destruction of fluorocyclopropenone is greatly accelerated by using shorter wavelength irradiation. Gas phase irradiation of fluoromaleic anhydride at room temperature leads only to difluoroacetylene as does treatment of the anhydride under flash vacuum pyrolysis conditions. Ab initio calculations are reported for fluoropropadienone, fluoro(ketenyl)carbene, and fluorocyclopropenone, and the results are compared with experiment.

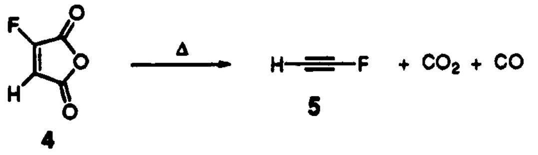
Difluoromaleic anhydride (**1**) is a convenient precursor to difluoropropadienone (**2**) under flash vacuum pyrolysis conditions, while under photochemical conditions it is a good source of difluorocyclopropenone (**3**).[1] The photochemical reaction works well under matrix isolation conditions[1] but can also be conducted on a semi-preparative scale at room temperature in the gas phase[2] (eq 1).



(1)

Because of our success in using **1** as a precursor to **2** and **3**, we have investigated the analogous chemistry of fluoromaleic anhydride (**4**).

Fluoromaleic anhydride was synthesized by the literature procedure.[3] Flash vacuum pyrolysis of fluoromaleic anhydride is reported to yield fluoroacetylene (**5**), carbon monoxide, and carbon dioxide.[4] We have repeated this reaction under a range of conditions and have obtained similar results (eq 2). There is no evidence for the formation of fluoropropadienone. This is in contrast to the thermal chemistry of **1** which cleanly gives **2** under similar conditions.



(2)

Irradiation (λ = 240 nm) of **1** under matrix isolation conditions produces difluorocyclopropenone (**3**) and small amounts of difluoroacetylene and carbon monoxide. Shorter wavelength irradiation converts **3** to difluoroacetylene and carbon monoxide. In a similar manner, an argon matrix of fluoromaleic anhydride (**4**) was prepared[5] (Figure 1)[6] and was irradiated at 240 nm. Initially, two primary photoproducts are formed in addition to CO_2 (Figure 2). One has bands at 2168, 1321, and 1102 cm^{-1} and is tentatively assigned as fluoro(ketenyl)carbene (**6**) based on comparison with calculated vibrational spectra. The bands assigned to **6** reach a small, maximum value after about 1 h of irradiation and then slowly begin to decrease as the photolysis is continued. The other primary photoproduct, assigned as fluorocyclopropenone (**7**), continues to increase until no starting anhydride **4** remains (Figure 3). The bands assigned to **7** are observed at 1899, 1872, 1652, 1229, 1227, 849, and 750 cm^{-1}. Secondary photoproducts consisting of fluoroacetylene and carbon monoxide are formed throughout the irradiation. Once all of **4** has reacted, continued irradiation using monochromatic light at 240 nm leads to the slow decomposition of **7** and the generation of more fluoroacetylene and carbon monoxide. This process can be greatly facilitated by using light from a medium-pressure mercury arc filtered through Vycor (λ > 220 nm) (Figure 4).[7] On the basis of integrated band intensities for fluoroacetylene and carbon monoxide before and after irradiation with the mercury arc through Vycor, we conclude that Figure 3 represents a 1:1:1 ratio of **7**:**5**:carbon monoxide. If we assume that all of the secondary photoproducts that are formed during the monochromatic irradiation arise from fluoro(ketenyl)carbene (**6**), then this implies that **4** is initially converted

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® Abstract published in *Advance ACS Abstracts,* October 1, 1995.

[1] Brahms, J. C.; Dailey, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8940.

[2] Jacobs, C. A.; Brahms, J. C.; Dailey, W. P.; Beran, K.; Harmony, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 115.

[3] Rausch, M. S.; Migel, R. E.; Castle, J. E. *J. Am. Chem. Soc.* **1959**, *81*, 2678.

[4] Middleton, W. J.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 803.

[5] The low temperature matrix isolation apparatus, IR spectrometer, and irradiation sources have been described previously. See: O'Gara, J. E.; Dailey, W. P. *J. Am. Chem. Soc.* **1992**, *114*, 3581.

[6] IR of fluoromaleic anhydride:Ar (1:1500): 1813.5, 1804.8, 1791.3, 1783.8, 1338.5, 1241.6, 1233.6, 1185.4, 998.1, 894.9, 789.8 cm^{-1}.

[7] IR of fluoroacetylene:Ar: 3344.4, 2237.8, 1063.4, 1062.2, 685.6, 657.4 cm^{-1}.

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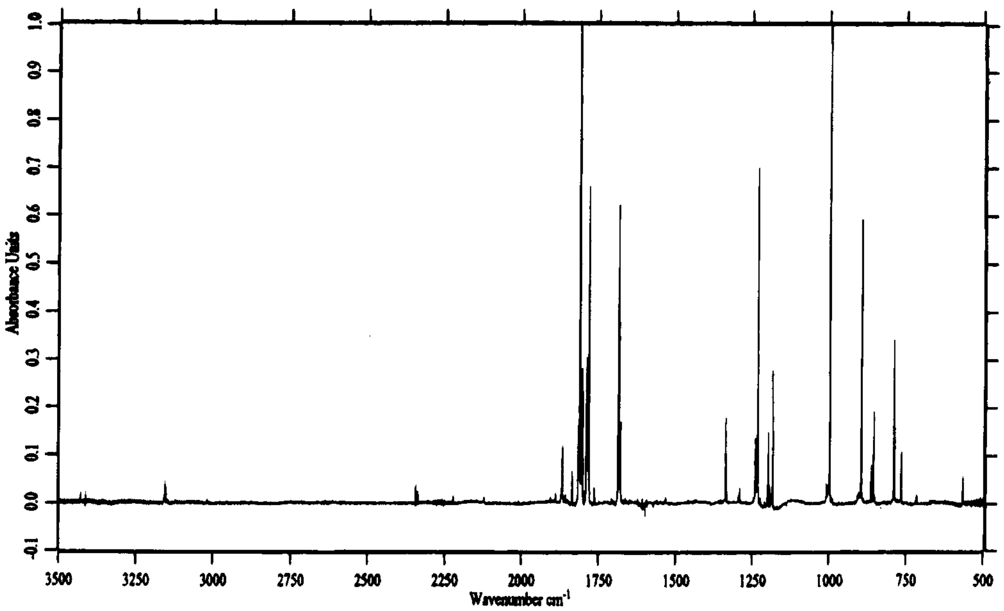


Figure 1. Matrix-isolated infrared spectrum (Ar, 11 K) of fluoromaleic anhydride (**4**).

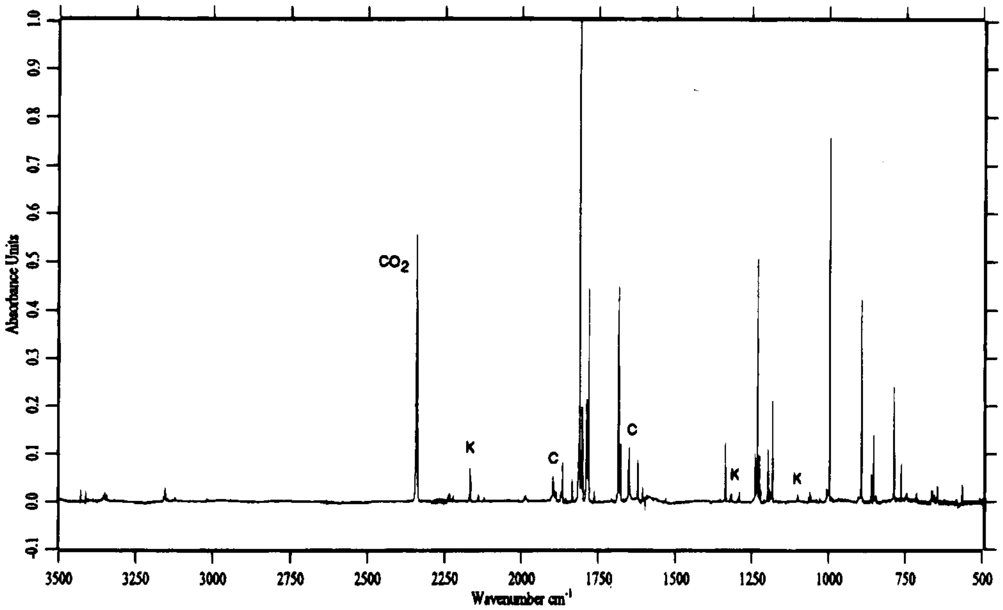
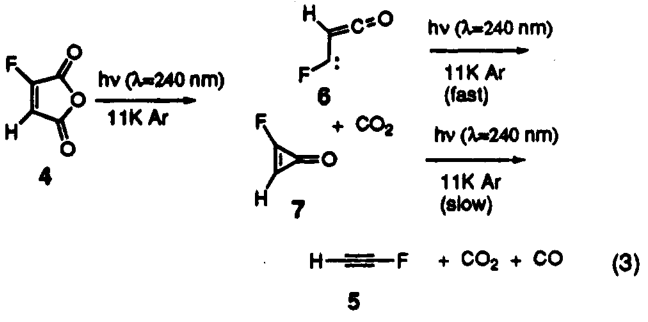
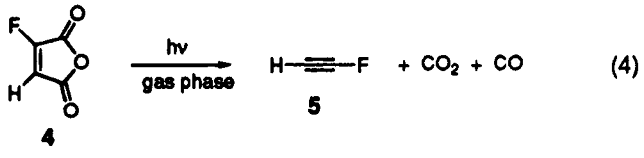


Figure 2. Matrix-isolated infrared spectrum (Ar, 11 K) of fluoromaleic anhydride (**4**) after 1 h of irradiation at λ = 240 nm. Bands marked K are assigned to fluoro(ketenyl)carbene (**6**), and bands marked C are assigned to fluorocyclopropenone (**7**).

to an equal amount of **6** and **7** (eq 3). Attempts to remove **7** intact from the matrix have not yet been successful.



Gas phase photolysis of difluoromaleic anhydride can be used to prepare quantities of difluorocyclopropenone for study, and we attempted to use these conditions for the preparation of fluorocyclopropenone (**7**). However, gas phase photolysis of **4** under similar conditions described for gas phase photolysis of **1** cleanly produced only fluoroacetylene, carbon monoxide and carbon dioxide (eq 4). There was no trace of **7** in the products.



Ab Initio Calculations

As an aid in these assignments, we have carried out ab initio molecular orbital calculations using the Gauss-

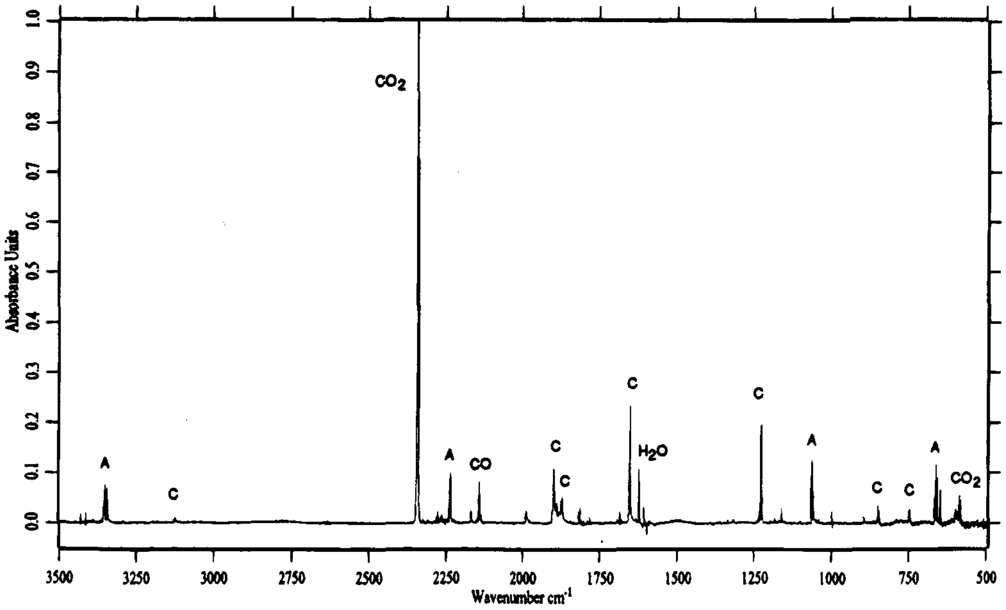


Figure 3. Matrix-isolated infrared spectrum (Ar, 11 K) of fluoromaleic anhydride after 8 h of irradiation at $\lambda = 240$ nm. Bands marked C are assigned to fluorocyclopropenone (**7**), and bands marked A are assigned to fluoroacetylene (**5**).

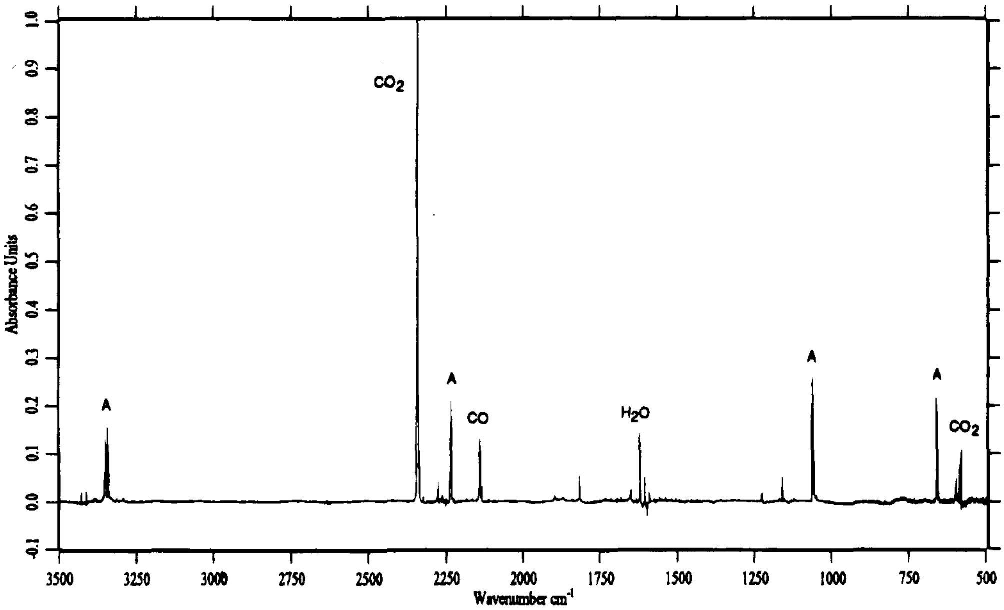


Figure 4. Matrix-isolated infrared spectrum (Ar, 11 K) of fluoromaleic anhydride after 8 h of irradiation at $\lambda = 240$ nm and 1 h of irradiation through Vycor ($\lambda > 220$ nm). Bands marked A are assigned to fluoroacetylene (**5**).

ian 92 program.[8] The structures were fully geometry optimized at the MP2(fixed core) level of theory using the 6-31G** basis set. Analytical frequency calculations were performed on the optimized structures and confirmed the nature of the stationary points. Single point energy calculations were performed at the MP4(sdtq,fixed core)/6-311(2df,2p) level of theory using the MP2(fc)/6-31G**-optimized geometries. The optimized structures and dipole moments for singlet fluoro(ketenyl)carbene (**6a** and **6s**), fluorocyclopropenone (**7**), and fluoropropadienone (**8a** and **8s**) are shown in Figure 5. The MP2(fc)/6-31G** and MP4(sdtq,fc)/6-311(2df,2p) total energies and the zero point vibrational energy (ZPE) at the MP2(fc)/6-31G** level of theory are shown in Table 1. All of the structures in Figure 5 are predicted to be planar. For both fluoro(ketenyl)carbene and fluoropropadienone, two isomers of similar energy were found. For fluoropropadienone, the isomer that has fluorine anti to the ketene group (**8a**) is calculated to be more stable than isomer **8s** by 0.8 kcal/mol. The kinked nature of the propadienone O=C=C=C unit is experimentally well established for both the parent compound[9] and the difluoroderivative.[10] Ab initio calculations reproduce the experimental results if a correlated wavefunction is used for the parent compound[11] while the HF/6-31G* level of theory is sufficient

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(8) Gaussian 92/DFT, Revision G.4: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P. Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1993.

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(10) Tam, H. S.; Harmony, M. D.; Brahms, J. C.; Dailey, W. P. *J. Mol. Struct.* **1990**, *223*, 217.

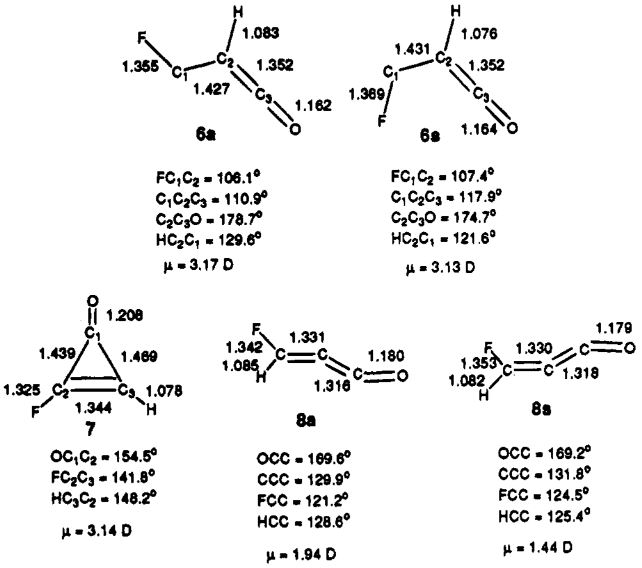

Figure 5. 5. Geometries and total energies of several singlet minima calculated at the MP2(fc)/6-31G** level. Bond lengths in angstroms, angles in degrees.

Table 1. Total Energies (Hartrees), Zero Point Vibrational Energies (at MP2(fc)/6-31G, kcal/mol), and Relative Energies (E(MP4) + ZPE, kcal/mol) of Several C_3FHO Isomers**[a]

	total energy and method			
structure	MP2(fc)/6-31G**	MP4(sdtq,fc)/ 6-311(2df,2p)	ZPE	rel *E*
6a	−289.071 22	−289.422 02	18.6	11.7
6s	−289.070 66	−289.421 01	18.7	12.6
7	−289.099 22	−289.442 44	19.5	0.0
8a	−289.122 06	−289.470 59	19.7	−17.5
8s	−289.121 83	−289.469 37	19.7	−16.7
9	−289.029 60	−289.382 42	17.4	35.6
10	−289.066 78	−289.417 56	18.3	14.4
11	−289.004 60	−289.360 08	17.5	49.7
12	−289.049 94	−289.400 99	17.5	24.0
13	−288.984 62	−289.337 70	15.2	61.4
14	−288.985 87	−289.339 59	15.5	60.5
FCCH	−176.067 58	−176.284 67	12.5	
CO	−113.021 21	−113.152 80	3.0	−0.9[b]

[a] 1 hartree = 627.5 kcal/mol. [b] Relative energy of FCCH + CO.

Table 2. Calculated (MP2(fc)/6-31G) and Observed Matrix-Isolated Infrared Vibrational Spectral Data for Fluorocyclopropenone (7)**

frequencies, cm^{-1}			intensities[a]	
calcd	scaled[b]	obsd	calcd	obsd
3330.8	3141	3123.7	6 (0.7)	0.9
2002.0	1908	1899.3	380 (43)	43
1872.3				
1716.2	1642	1652.9	234 (26)	31
1261.4	1220	1229.1	126 (14)	19
1227.6				
1097.8	1069		13 (1)	
852.8	841		11 (1)	
844.5	834	849.3	52 (6)	4
752.5	748	750.0	54 (6)	2
640.2	644		5 (1)	
601.4	607		1 (0)	
282.5	311		1 (0)	
276.5	306		4 (1)	

[a] The calculated intensities are in kilometers per mole. Observed intensities and those in parentheses are normalized to 100. [b] Scaled according to eq 6 (see text).

Table 3. Calculated (MP2(fc)/6-31G) Infrared Vibrational Spectrum for Fluoropropadienone (8s)**

frequencies, cm^{-1}		intensities[a]
calcd	scaled[b]	calcd
3286.8	3100	15
2231.6	2120	850
1769.2	1692	160
1428.4	1375	3
1161.6	1128	187
966.7	947	9
957.6	938	3
665.7	668	61
639.7	643	31
513.1	526	16
245.9	278	2
122.2	163	1

[a] In kilometers per mole. [b] Scaled according to eq 6 (see text).

Table 4. Calculated (MP2(fc)/6-31G) Infrared Vibrational Spectrum for Fluoropropadienone (8a)**

frequencies, cm^{-1}		intensities[a]
calcd	scaled[b]	calcd
3242.3	3059	15
2240.5	2129	884
1766.7	1690	165
1400.8	1350	22
1215.2	1177	260
1046.6	1022	93
924.6	908	2
614.0	620	12
564.1	573	3
502.3	516	9
153.5	193	4
151.6	191	3

[a] In kilometers per mole. [b] Scaled according to eq 6 (see text).

to reproduce the structure of the difluoro derivative.[12] Only singlet fluoro(ketenyl)carbene was examined since it is known that fluorine directly attached to a carbene carbon strongly favors the singlet state compared with the triplet.[13] For singlet fluoro(ketenyl)carbene, the isomer with fluorine anti to the ketene unit (**6a**) is more stable than isomer **6s** by 0.9 kcal/mol. The vibrational spectra for all of these local minima were calculated analytically and are given in Tables 2–6.

The transition structure (**9**) for the interconversion of **6a** and **6s** by rotation of the C_1-C_2 bond was located and is shown in Figure 6. At the MP2(fc)/6-31G** + ZPE level of theory, the barrier for the interconversion of **6a** and **6s** is calculated to be 25 kcal/mol. The reason for this large rotational barrier can be understood through an analysis of the structural changes that occur upon rotation. In the planar conformations **6a** and **6s**, the vacant p orbital of the singlet carbene carbon can interact through resonance with one of the lone pairs of electrons from oxygen. For **6a**, this interaction can be expressed in resonance language as a contribution from valence bond structure **6c** (eq 5). An analogous structure can be drawn for **6s**. In transition structure **9**, the vacant p-orbital is perpendicular to the plane containing the oxygen lone pairs, and such a resonance interaction is not possible. The importance of this interaction can be observed by examining the changes in bond lengths of **6a** and **6s** compared with **9**. Bonds C_1-C_2 and C_3-O are calculated to be much shorter in both **6a** (1.427 and 1.162

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(11) (a) Farnell, L.; Radom, L. *Chem. Phys. Lett.* **1982**, *91*, 373. (b) Taylor, P. R. *J. Comput. Chem.* **1984**, *5*, 589. (c) Brown, R. D.; Dittman, R. G. *Chem. Phys.* **1984**, *103*, 5711.

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Table 5. Calculated (MP2(fc)/6-31G) Infrared Vibrational Spectrum for Fluoro(ketenyl)carbene (6a)**

frequencies, cm^{-1}			intensities[a]	
calcd	scaled[b]	obsd	calcd	obsd
3272.3	3086		8 (0.6)	
2235.8	2125	2168	565(44)	60
1367.1	1319	1321	261 (20)	21
1219.2	1181		46 (4)	
1155.0	1122	1102	192 (15)	13
1075.7	1048		138 (11)	
717.4	715		40 (3)	
582.1	590		3 (0)	
579.7	588		23 (2)	
458.8	475		4 (0)	
166.9	204		4 (0)	
153.9	193		4 (0)	

[a] The calculated intensities are in kilometers per mole. Observed intensities and those in parentheses are normalized to 100. [b] Scaled according to eq 6 (see text).

Table 6. Calculated (MP2(fc)/6-31G) Infrared Vibrational Spectrum for Fluoro(ketenyl)carbene (6s)**

frequencies, cm^{-1}			intensities[a]	
calcd	scaled[b]	obsd	calcd	obsd
3348.0	3157		17(1)	
2214.0	2105	2168	567(47)	60
1389.1	1339	1321	247(21)	21
1174.2	1139	1102	191(16)	13
1125.2	1094		29(2)	
1013.0	990		62	
757.5	752		8	
691.6	692		22	
608.2	614		35	
419.1	439		4	
215.6	249		8	
149.3	188		3	

[a] The calculated intensities are in kilometers per mole. Observed intensities and those in parentheses are normalized to 100. [b] Scaled according to eq 6 (see text).

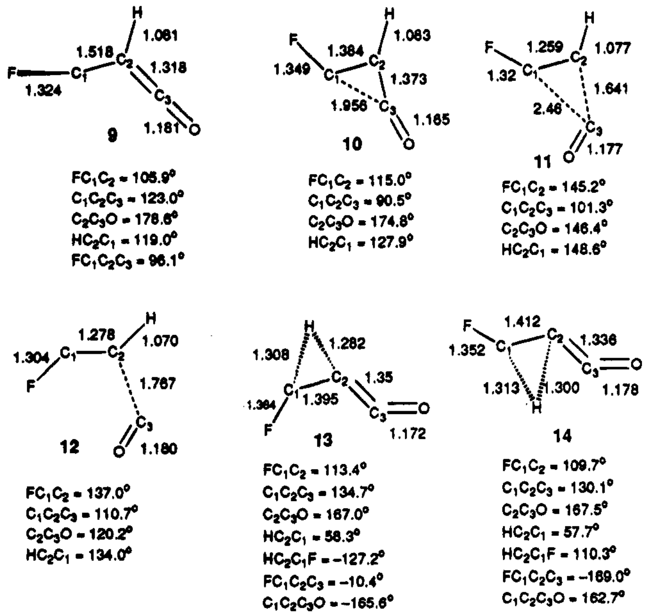
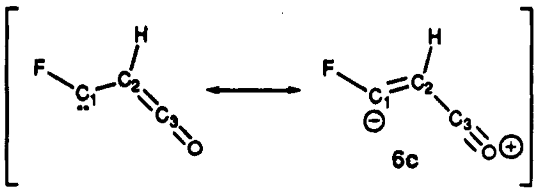


Figure 6. Geometries and total energies of several singlet transition structures calculated at the MP2(fc)/6-31G** level. Bond lengths in angstroms, angles in degrees.

Å) and **6s** (1.431 and 1.164 Å) than in **9** (1.518 and 1.181 Å), while bonds C_1–F and C_2–C_3 are much shorter in **9** (1.324 and 1.318 Å) than in both **6a** (1.355 and 1.352 Å) and **6s** (1.369 and 1.352 Å). These large changes in bond lengths are also accompanied by a large change in energy.



(5)

The significant structural and energetic changes that occur upon bond rotation indicate that resonance structures such as **6c** are very important contributors to the resonance hybrid. The ketenylcarbene is reminiscent of alkoxycarbenes which exhibit the same type of rotational barriers and delocalization of an oxygen lone pair into the carbene vacant p-orbital.[14] Indeed, ketenylcarbene **6** can be considered to be a vinylogous oxycarbene.

Several other transition structures were located at the geometry optimized MP2(fc)/6-31G** level of theory and are shown in Figure 6. For each structure, frequency calculations confirmed that it was a transition structure. Additionally, the identities of the two minima which were interconnected by each transition structure were confirmed by the intrinsic reaction coordinate (IRC) method.[15] MP2(fc)/6-31G** and MP4(sdtq,fc)/6-311(2df,2p) total energies and zero point vibrational energies (ZPE) for the transition structures are given in Table 1. Structure **10** corresponds to the transition structure for ring closure of fluoro(ketenyl)carbene **6a** to fluorocyclopropenone (**7**). At the MP4(sdtq,(fc))/6-311(2df,2p)//MP2(fc)/6-31G** + ZPE level of theory, the barrier to ring closure of **6a** to **7** is calculated to be only 2.7 kcal/mol. Transition structure **11** corresponds to the loss of carbon monoxide from cyclopropenone **7** leading to fluoroacetylene and carbon monoxide. The calculated barrier is 49.7 kcal/mol. Transition structure **12** corresponds to carbene **6s** fragmenting to carbon monoxide and fluoroacetylene. The barrier is calculated to be 11.4 kcal/mol. Despite repeated efforts, we were unable to locate a transition structure that corresponded to loss of carbon monoxide from carbene **6a**. All attempts led to transition structure **11** which interconnects **7** and fluoroacetylene plus carbon monoxide. Transition structure **13** corresponds to the hydrogen atom migration in carbene **6s** to produce fluoropropadienone **8s**. The calculated barrier is 48.8 kcal/mol. Transition structure **14** corresponds to the hydrogen atom migration in carbene **6a** to produce fluoropropadienone **8a**. The calculated barrier is also 48.8 kcal/mol. The relationships between these transition structures and the various minima which they interconnect are illustrated in Scheme 1.

Discussion

During the pyrolysis of fluoromaleic anhydride (**4**), the initial loss of carbon dioxide is expected to produce carbene **6** as the first intermediate. Experimentally, only fluoroacetylene, carbon monoxide, and carbon dioxide are observed as products. There is no evidence for the formation of fluoropropadienone (**8**). The transition structure calculations are consistent with these results. The conversion of carbene **6a** to fluorocyclopropenone (**7**) via transition structure **10** and then to fluoroacetylene and carbon monoxide via transition structure **11** is

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(14) Sheridan, R. S.; Moss, R. A.; Wilk, B. K.; Shen, S.; Wlostowski, M.; Kesselmayer, M. A.; Subramanian, R.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1988**, *110*, 7563.

(15) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

Scheme 1

$$\begin{tikzcd}
\mathbf{8a} \arrow[d, harpoon, shift left] & & \mathbf{8s} \arrow[d, harpoon, shift left] \\
{[\,\mathbf{13}\,]^{\ddagger}} \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] & & {[\,\mathbf{14}\,]^{\ddagger}} \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] \\
\mathbf{6a} \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] \arrow[r, harpoon, shift left] & {[\,\mathbf{9}\,]^{\ddagger}} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & \mathbf{6s} \arrow[l, harpoon, shift left] \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] \\
{[\,\mathbf{10}\,]^{\ddagger}} \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] & & {[\,\mathbf{12}\,]^{\ddagger}} \arrow[u, harpoon, shift left] \arrow[d, harpoon, shift left] \\
\mathbf{7} \arrow[u, harpoon, shift left] \arrow[r, harpoon, shift left] & {[\,\mathbf{11}\,]^{\ddagger}} \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] & \mathrm{FCCH} + \mathrm{CO} \arrow[l, harpoon, shift left] \arrow[u, harpoon, shift left]
\end{tikzcd}$$

calculated to have a lower barrier (38 kcal/mol) than does conversion of **6a** to fluoropropadienone **8a** via transition structure **13** (49 kcal/mol). Likewise, the barrier for conversion of carbene **6s** to fluoropropadienone **8s** via transition structure **14** is also calculated to be 49 kcal/mol. On the other hand, carbene **6s** has a barrier of only 11 kcal/mol for fragmentation to fluoroacetylene and carbon monoxide via transition structure **12**. Given that the barrier for the interconversion of carbenes **6a** and **6s** is 25 kcal/mol, the formation of fluoroacetylene and carbon monoxide is predicted to take place via transition state **12** whether starting with **6a**, **6s**, or **7**.

Of the two primary photoproducts that arise during the monochromatic irradiation of fluoromaleic anhydride (**4**) under matrix isolation conditions, the less photolabile species can be assigned as fluorocyclopropenone (**7**) with a high degree of certainty. This assignment is based on a comparison of the observed IR spectrum with that calculated for **7** (Table 2). The calculated band positions for **7** match the experimentally observed ones well (average error = 10 cm^{-1}) if the calculated values are scaled using eq 6. We have recently reported that eq 6

$$\nu_{\mathrm{obsd}} = (0.928)\nu_{\mathrm{calcd}} + 50\ \mathrm{cm}^{-1} \qquad (6)$$

may be used to bring MP2(fc)/6-31G** calculated frequency values into good agreement with those observed for cyclopentadienone and azacyclopentadienone under matrix isolation conditions.[16] Limited testing has shown that eq 6 can be applied to other systems with comparable results.

The experimental relative intensities also match the calculated values well. The clean photochemical conversion of **7** to **5** and carbon monoxide under conditions similar to those needed for fragmentation of difluorocyclopropenone is also good evidence in favor of the assignment of this primary photoproduct to **7**. The failure to isolate **7** under ambient conditions may be due to the predicted facile ring opening of **7** to **6a** via transition structure **10** which is calculated to be 14.4 kcal/mol.

Initially, the other more photochemically labile primary photoproduct was speculated to be fluoropropadienone. This was based on the IR band observed at 2168 cm^{-1} which is in the correct region for a ketene or methyleneketene vibration. However, fluoropropadienone (both **8a** and **8s**) is calculated (Tables 3 and 4) to have a major IR band around 1700 cm^{-1}, and this could not be located in the experimental spectrum. In addition, the relative intensities of the bands experimentally observed at 1321 and 1102 cm^{-1} were not well reproduced in the calculated spectra of either isomer (**8a** or **8s**) of fluoropropadienone. This suggested that some other species was responsible for the IR bands assigned to the second primary photoproduct.

Another plausible primary photoproduct that contains the ketene functional group is fluoro(ketenyl)carbene (**6**). We imagined that photolysis of **4** generates both **6a** and **6s** and that **6a** quickly ring closes to generate fluorocyclopropenone (**7**). Irradiation of the remaining **6s** might be expected to lead to decomposition to fluoroacetylene and carbon monoxide since this conformation of the carbene **6** cannot lead directly to **7**. Ab initio calculated IR spectra along with the values scaled according to eq 6 for both of the carbene isomers **6a** and **6s** are compared with the experimental values in Table 5 and Table 6, respectively. In both cases, the scaled frequencies and relative intensities were in reasonable agreement with the experimental values. Because of the low photostationary concentration of the intermediate, we were not able to conclusively locate other bands in the experimental spectrum that could be attributed to the second primary photoproduct. However, we believe that the evidence strongly favors the assignment of the second primary photoproduct to **6**. Moreover, based on our ab initio calculations, isomer **6a** is expected to have an extremely low barrier (2.7 kcal/mol) for ring closure to **7** and therefore would not be expected to be stable under the reaction conditions. On the other hand, isomer **6s** does not have a low energy thermal reaction pathway, either for ring closure to **7** or isomerization to **6a** and, therefore, would be expected to be stable under the matrix isolation conditions. Additionally, the relatively low barrier (12.3 kcal/mol) for fragmentation of **6s** to fluoroacetylene and carbon monoxide via transition structure **12** is consistent with the chemistry observed under the matrix conditions. Thus, we assign the second primary photoproduct as carbene **6s**. A summary of the proposed reaction sequence is shown in Scheme 2.

Photochemically, matrix isolated fluoromaleic anhydride (**4**) is converted to a 1:1 mixture of fluoro(ketenyl)carbene isomers **6a** and **6s**. Isomer **6a** quickly ring closes to fluorocyclopropenone (**7**) while isomer **6s** is thermally stable under the reaction conditions. Continued irradiation at $\lambda = 240$ nm leads to the facile decarbonylation of **6s** and the formation of fluoroacetylene. Under these photochemical conditions, **7** is very slowly converted to the same products. However, shorter wavelength irradiation ($\lambda > 220$ nm) quickly converts **7** to fluoroacetylene and carbon monoxide.

Finally, it is interesting that we can find no evidence for the formation of fluoropropadienone in either the photochemical or thermal reaction of fluoromaleic anhydride even though fluoropropadienone is predicted to be 17 kcal/mol more stable thermodynamically than fluorocyclopropenone.

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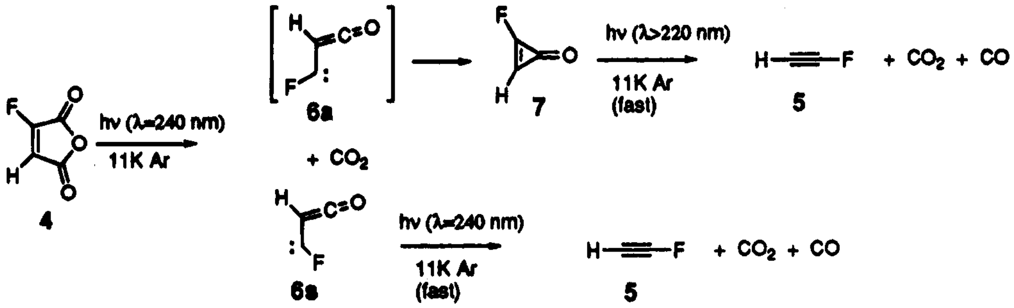
(16) Yokotsuji, D. L. S.; Dailey, W. P.; Kende, A. S.; Birzan, L.; Liu, K. *J. Phys. Chem.*, in press.

Scheme 2



Summary and Conclusions

Irradiation of fluoromaleic anhydride (**4**) under matrix isolation conditions produces fluoro(ketenyl)carbene **6s** and fluorocyclopropenone (**7**) as primary photoproducts based on comparison with ab initio calculations. While the observed spectrum for the carbene can be matched well to that calculated for either **6a** and **6s**, the carbene is assigned to **6s** based on the fact that ab initio calculations predict a very small barrier for ring closure of **6a** to **7**. There is a substantial barrier calculated for the interconversion of **6a** and **6s**. Under conditions for its photochemical generation, carbene **6s** is efficiently converted to fluoroacetylene and carbon monoxide and never reaches a significant concentration. Fluorocyclopropenone (**7**) is converted more slowly under the original photochemical conditions but is quickly decomposed using a medium pressure mercury arc through Vycor. Attempts to isolate **7** in pure form have so far been unsuccessful.

Acknowledgment. W.P.D. thanks the National Science Foundation for financial support, the Alfred P. Sloan Foundation for a research fellowship (1990–1994), and Carolyn Jacobs for performing some preliminary experiments.

JO951368V