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Mercury 6($^3P_1$) Photosensitization of Mono- and Difluoroethylenes. Correlation of Mechanism with Calculated Molecular Orbital Energy Levels

**O. P. Strausz,* R. J. Norstrom,[1a] D. Salahub,[1a]
R. K. Gosavi,[1a] H. E. Gunning,[1a] and I. G. Csizmadia[1b]**

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, and the University of Toronto, Toronto, Ontario, Canada.

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Abstract: The triplet mercury photosensitized decompositions of vinyl fluoride, 1,1-difluoroethylene, and *cis*- and *trans*-1,2-difluoroethylene proceed by molecular elimination of HF *via* an excited molecule mechanism producing the corresponding acetylene. Cis ⇄ trans isomerization occurs on deactivation, but structural isomerization is absent. Extended Hückel MO calculations have been carried out for ethylene, the haloethylenes, the corresponding acetylenes, and the intermediate carbenes implicated in the decomposition of these olefins. An attempt to correlate the decomposition mechanism with state energy levels, as calculated by the LCAO–MO method, is described.

Triplet mercury photosensitization of olefins leads to the promotion of the olefin to its lowest lying (Π,Π*) triplet state.[2] Detailed kinetic studies have shown that in the ensuing reactions at least one, and possibly more, additional electronic state is involved. The exact nature of these excited states has not yet been established, though the ground or some excited state of the isomeric ethylidene structure is strongly implicated.[3] The vibrationally excited ground state has also been suggested as the principal decomposition state.[4] This could presumably be reached through the sequence[5] shown below.

$$\text{triplet ethylene} \xrightarrow{\text{isomerization}} \text{ground state triplet ethylidene} \xrightarrow[\text{crossing}]{\text{intersystem}} \text{excited singlet ethylidene} \xrightarrow{\text{isomerization}} \text{ground state singlet ethylene}$$

In the case of ethylene the excited molecule, unless deactivated by collision, undergoes molecular hydrogen elimination and, to a minor extent, hydrogen atom loss. The occurrence of H atom loss, however, has recently been questioned.[6]

In sharp contrast to this, the decomposition of tetrafluoroethylene consists entirely of carbon–carbon bond cleavage[7] producing two CF_2, and the retarding effect of pressure becomes noticeable only at relatively high pressures. This change in reactivity upon fluorination is related to the alteration of the electronic properties of the molecule. Successive fluorination progressively decreases the length of both the C—F and C=C linkages. From MO considerations, Peters[8] concluded that charge transfer from carbon to fluorine is the primary cause of these bond shortenings. In spite of the shortening of the C=C bond, the bond

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* Address correspondence to this author at the University of Alberta.

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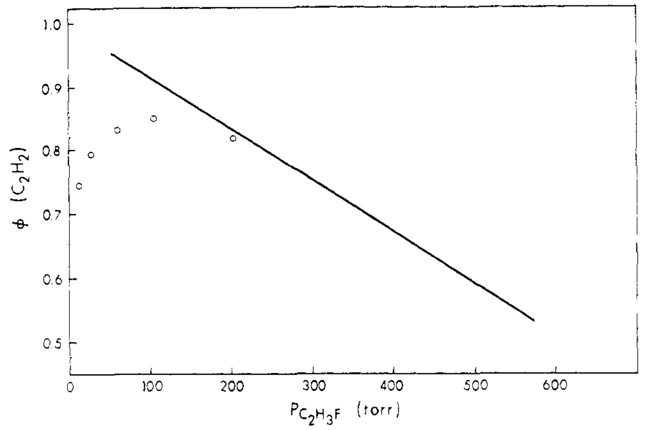

Figure 1. Quantum yields of acetylene formation as a function of MFE pressure from the mercury photosensitization of MFE: ——, from ref 3; ○, from present work.

dissociation energy progressively declines upon fluorination, and this has been ascribed to the change in the promotion energy of the carbon atom during the rupture process. Indeed, Simons[9] suggest that the thermal dissociation of tetrafluoromethylene into two difluoromethylenes is a nonadiabatic process and that the long-wavelength photolysis should result in dissociation into two singlet ground state difluoromethylenes along an essentially repulsive surface.

Among the partially fluorinated ethylenes, the mercury photosensitization of only vinyl fluoride has been reported in the literature.[4a] One relevant reaction,[10] the mercury photosensitization of vinyl chloride, has also been studied. In both systems a marked shortening of the decomposition lifetime as compared to ethylene has been observed and the exclusive mode of decomposition of the excited molecule was molecular hydrogen halide elimination. In the vinyl fluoride reaction the zero-pressure extrapolated quantum yield of excited molecule decomposition was reported to be unity, while, in the more complex reaction of vinyl chloride, only a fraction of the excited molecules appeared to undergo decomposition. It is important to note that organically bound halogen atoms are efficient quenchers of excited mercury atoms, with the exception of the fluorine atom, which is completely inert. For this reason fluoroethylenes are particularly suited to mercury photosensitization studies.

In order to learn more about the triplet state behavior of partially fluorinated ethylenes, we have examined the triplet mercury and triplet cadmium photosensitization of all partially fluorinated ethylenes. The present article describes the triplet mercury plus monofluoroethylene (MFE) and difluoroethylene (DFE) systems and gives an account of an attempt made to generalize and correlate the experimental results with extended Hückel molecular orbital (EHMO) state-energy levels. Parts II and III of this series deal with the trifluoroethylene (TFE) system.

Experimental Section

Conventional high-vacuum techniques were employed. The reaction vessel was a 10 × 5 cm cylindrical quartz cell, which was irradiated by a Hanovia No. 687A45 low-pressure Hg resonance lamp through a Vycor 7910 filter.

Absorbed light intensities were determined by propane actinometry ($\phi(H_2) = 0.51$). For the low-pressure quantum yield measurements it was necessary to correct for the Lorentz broadening of the mercury resonance line. Appropriate correction factors were obtained by measuring the amount of light absorbed as a function of gas pressure in the cell. This was achieved by placing a 1P28 photomultipler equipped with a 2537-Å interference filter behind the cell. The photomultiplier was powered by a Phillips GM4561 stabilized power supply, and the readout was done with a Hewlett-Packard 3444 digital voltmeter.

Correction functions obtained for the four gases propane, MFE, DFE, and TFE had the form $1/f = A + B/P$, where f is the fraction of incident intensity of 2537-Å radiation absorbed and P is the pressure in Torr. The value of A was 1.000 ± 0.004 for all four gases studied. The values of B were 3.00, 2.67, 2.89, and 2.94, respectively, for C_3H_8, C_2H_3F, $C_2H_2F_2$, and C_2HF_3.

Materials. MFE and 1,1-DFE (Matheson) were degassed at −196° and distilled from −160° (isopentane slush). The 1,2-DFE (Peninsular) was a mixture of the cis and trans isomers. After degassing, the material was distilled from −130° (*n*-pentane slush) and the isomers were separated by preparative gc on an 18-ft 20% dibutyl maleate on firebrick (60–80) column. The retention times of the trans and cis isomers were 6.7 and 13.2 min, respectively, at a He flow rate of 47 ml/min and at 25°.

Analytical Procedure. The acetylene product of the MFE reaction was distilled at −160°, where MFE has a substantial vapor pressure. The distillate was then analyzed by gc on a 4-ft high activity silica gel column at a He flow rate of 50 ml/min and at 35°. The process was repeated in each experiment until no acetylene could be detected in the distillate by gc.

With the difluoroethylenes, the monofluoroacetylene product could not be separated from the reactant by distillation; therefore, the whole reaction mixture was passed through the gc. For the 1,1-DFE a 6-ft medium-activity silica gel column was used with 90-ml/min flow rate of He at 25°. The 1,2-DFE reaction mixture was analyzed on the dibutyl maleate column described above. Some difficulty was encountered in runs with the trans isomer in that the reactant peak tailed into the cis-product peak; this necessitated splitting the reaction mixture into portions and running these separately.

Results

The only retrievable product of the MFE reaction was acetylene, identified by gc retention time and mass spectrometry. Water was also detected but not measured quantitatively. The water evidently arose from the reaction of hydrogen fluoride with the quartz surface of the reaction vessel.

The quantum yield of acetylene formation has been measured as a function of MFE pressure. The data are given in Figure 1 in comparison with Trobridge and Jennings' previous measurements.[4a] At 200 Torr of pressure, the quantum yield reported here agrees with Trobridge and Jennings' value, but at lower pressures a small discrepancy appears. The zero-pressure extrapolated quantum yield of decomposition appears to be unity or near unity.

Addition of small concentrations of nitric oxide to the system did not affect the quantum yield of acetylene formation, indicating that it is a molecular process

$$C_2H_3F + Hg^* \longrightarrow C_2H_3F^* + Hg$$

$$C_2H_3F^* \longrightarrow C_2H_2 + HF$$

All three isomeric difluoroethylenes, the 1,1- and the *cis*- and *trans*-1,2-DFE, afforded monofluoroacetylene as the only principal decomposition product; this was identified by mass spectrometry. In addition, the 1,2-difluoro compounds also yielded their geometrical isomers. In the 1,1-DFE decomposition, a small peak eluted on the gc column shortly after C_2HF. It appeared only in low-pressure runs and in small yields.

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An attempt was made to identify it, but without success.

Table I contains the quantum yield of C_2HF formation as a function of substrate pressure for 1,1-DFE.

Table I. Quantum Yields of Monofluoroacetylene from the Mercury Photosensitization of 1,1-DFE as a Function of Pressure

P(1,1-DFE), Torr	Exposure time, min	$1/f^a$	$\phi(C_2H_2)$
10.6	67	1.276	0.744
12.2	30	1.240	0.737
17.4	120	1.168	0.723
22.9	100	1.128	0.716
27.1	133	1.108	0.706
32.5	120	1.092	0.703
40.8	220	1.072	0.690
60.6	240	1.041	0.654
76.3	345	1.039	0.621
86.6	268	1.035	0.601
157.0	540	1.019	0.491

[a] Lorentz broadening correction factor; $I_a = 2.68 \times 10^{15}$ quanta/sec.

Similar data for the 1,2 isomers, along with the quantum yield of the geometrical isomerization, are given in Tables II and III. The quantum yields of geometrical isomerization are identical in the cis and trans systems, indicating that the two isomers form with equal probability from a common intermediate. Therefore the quantum yield of the isomerization reaction is taken as twice that of the observable isomer formation.

Table II. Quantum Yields of Product Formation from the Mercury Photosensitization of *trans*-1,2-DFE as a Function of Pressure

P(*trans*-DFE), Torr	Exposure time, min	$1/f^a$	2ϕ-(isomer)	$\phi(C_2HF)$
10.5	60.0	1.278	0.042	0.700
16.5	60.0	1.177		0.658
17.8	60.0	1.164	0.053	0.707
23.6	57.4	1.124	0.055	0.723
28.3	60.0	1.104	0.077	0.717
32.2	60.0	1.091	0.082	0.636
34.3	60.0	1.086	0.083	0.700
44.6	60.0	1.066	0.108	0.686
45.1	60.0	1.065	0.100	0.647
62.0	60.0	1.047	0.129	0.674
68.7	60.0	1.043	0.148	0.648

[a] Lorentz broadening correction factor; $I_a = 1.11 \times 10^{15}$ quanta/sec.

Table III. Quantum Yields of Product Formation from the Mercury Photosensitization of *cis*-1,2-DFE as a Function of Pressure

P(*cis*-DFE), Torr	Exposure time, min	$1/f^a$	2ϕ(isomer)	$\phi(C_2HF)$
15.4	31.8	1.189	0.043	0.722
19.6	32.6	1.149	0.049	0.717
23.0	34.6	1.128	0.047	0.698
29.0	35.6	1.101	0.068	0.692
44.6	31.1	1.066	0.100	0.683
54.2	30.4	1.055		0.667
95.2	60.0	1.032	0.202	0.547
113.6	60.1	1.027	0.260	0.585
116.7	60.0	1.026		0.562
174.5	60.0	1.018	0.354	0.452
230.0	63.5	1.013	0.443	0.382
282.8	60.0	1.011	0.493	0.370
328.5	60.0	1.010		0.315

[a] Lorentz broadening correction factor; $I_a = 1.11 \times 10^{15}$ quanta/sec.

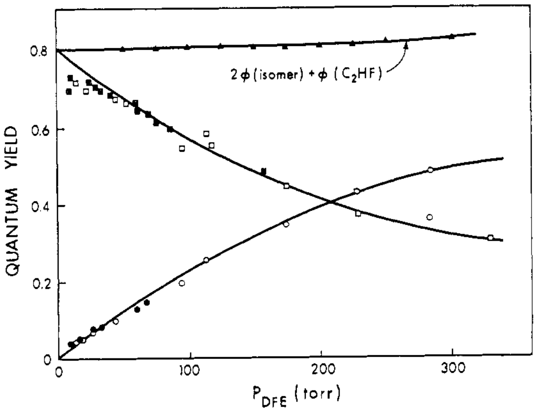

Figure 2. Quantum yields of product formation as a function of reactant pressure from the mercury photosensitization of difluoroethylenes: ■, $\phi(C_2HF)$ from 1,1-DFE; □, from *cis*-1,2-DFE; ⊠, from *trans*-1,2-DFE; ○, 2ϕ(isomer) from *cis*-1,2-DFE; ●, from *trans*-1,2-DFE; ▲, sum of 2ϕ(isomer) and $\phi(C_2HF)$ from *cis*- and *trans*-1,2-DFE.

The data from Tables I–III are plotted in Figure 2. It may be seen that the decompositions of all three isomeric difluoroethylenes exhibit similar pressure dependences. The quantum yield of C_2HF formation decreases, and that of geometrical isomerization increases, with increasing pressure. The sum of the two quantum yields appears to rise slowly with pressure from a value of 0.80 at zero pressure to about 0.86 at 283 Torr, the highest pressure employed. This increase in the yield of recovered products may be due either to secondary photolysis of monofluoroacetylene at lower pressures or to the occurrence of an additional mode of decomposition which is gradually suppressed at higher pressures.

Molecular Orbital Calculations. Molecular orbital and state energies were calculated for the molecules experimentally investigated to date, with the goal of obtaining a clearer understanding of the complex phenomena occurring in the mercury photosensitization of ethylene and halogenated ethylenes. The calculations were also extended to include isomeric species of the reactant molecules as well as their possible decomposition products.

One-electron energies were calculated by Hoffmann's EHMO method.[11] Characteristics of the Slater-type atomic orbitals[12] and structural parameters[13,14] used in the computations were taken from the literature.

The results are presented in Tables IV–VI. Table IV gives the ground state and the lowest excited state energies for the planar and skew forms of ethylene, fluoroethylenes, and vinyl chloride. In all cases the planar geometry is more stable than the skew in the

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Table IV. Energies of Ethylene and Fluoroethylenes by EHMO Calculations

Molecule	Conformation	Energy, kcal Ground state	First excited state
$H_2C{=}CH_2$	Planar	−4604	−4486
	Skew	−4520	−4520
$H_2C{=}CHF$	Planar	−8300	−8179
	Skew	− 8235	−8208
$HFC{=}CFH$	Planar (trans)	−11985	−11860
	Planar (cis)	−11988	−11863
	Skew[a]	−11897	−11895
$H_2C{=}CF_2$	Planar	−11995	−11864
	Skew[b]	−11944	−11892
$HFC{=}CF_2$	Planar	−15677	−15546
	Skew	−15607	−15584
$F_2C{=}CF_2$	Planar	−19362	−19227
$H_2C{=}CHCl$	Planar	−6993	−6873
	Skew	−6936	−6909

[a] CH_2 plane is perpendicular to the CCF_2 plane. [b] CHF plane is perpendicular to the CCF_2 plane.

Table V. Energies of Carbene Intermediates of Ethylene and Haloethylenes by EHMO Calculations

Molecule	Energy, kcal Ground state	First excited state	$X{-}\ddot{C}{-}Y$ angle, deg
$H{-}\ddot{C}{-}CH_3$	−4523	−4508	124
$H{-}\ddot{C}{-}CH_2F$	−8237	−8214	126
$H{-}\ddot{C}{-}CHF_2$	−11926	−11919	180
$H{-}\ddot{C}{-}CF_3$	−15629	−15621	132
$H{-}\ddot{C}{-}CH_2Cl$	−6934	−6916	180
$F{-}\ddot{C}{-}CH_3$	−8221	−8180	106
$F{-}\ddot{C}{-}CH_2F$	−11927	−11886	104
$F{-}\ddot{C}{-}CHF_2$	−15611	−15583	106
$F{-}\ddot{C}{-}CF_3$	−19321	−19293	104
$Cl{-}\ddot{C}{-}CH_3$	−6916	−6879	106
$:CH_2$	−2246	−2246	180
$:CH_2$	−2245	−2239	140
$:CHF$	−5922	−5890	102
$:CF_2$	−9623	−9538	105
$:CHCl$	−4630	−4603	103
$:C{=}CH_2$	−3764	−3713	116
$:C{=}CHF$	−7442	−7406	120
$:C{=}CF_2$	−11127	−11095	110
$:C{=}CHCl$	−6111	−6066	120

Table VI. Energies of Acetylene, Haloacetylenes, and F_2, H_2, HCl, and HF by EHMO Calculations

Molecule	Energy, kcal Ground state	First excited state
$HC{\equiv}CH$	−3859	−3709
$HC{\equiv}CF$	−7521[a]	−7362
	−7517[b]	−7358
$HC{\equiv}CCl$	−6220	−6072
$FC{\equiv}CF$	−11171[a]	−11008
	−11165[b]	−11001
$H{-}H$	−830	
$F{-}F$	−8043	
$H{-}F$	−4475	
$H{-}Cl$	−3153	

[a] C—F = 1.34 Å. [b] C—F = 1.30 Å.

ground state, while in the first excited state, the energy levels are inverted. It is also interesting to note that, with 1,2-DFE, the cis isomer is slightly more stable than the trans in the ground and first excited states.

Calculated state energy levels of the ethylidene-, vinylidene-, and methylene-type intermediates are given in Table V. The energies of ground state ethylidenes are the minimum values with respect to the $:C<$ bond angles. Energy variations with $H{-}\ddot{C}{-}$ bond distances for $H{-}\ddot{C}{-}CH_3$ and $H{-}\ddot{C}{-}CH_2F$ and energy variation with $F{-}\ddot{C}{-}$ distances for $F{-}\ddot{C}{-}CH_3$ were calculated at the equilibrium $:C<$ bond angles.[15]

The energy levels of the decomposition products and the acetylene structures and their companion diatomic molecules are listed in Table VI.

Discussion

The triplet mercury photosensitized reactions of mono- and difluoroethylenes follow the familiar pattern established for ethylene with some individual variation. Energy transfer promotes the molecule to an excited triplet state with an excess of vibrational energy. The only significant mode of decomposition is molecular HF loss, H_2 elimination does not occur. Cis ⇄ trans isomerization takes place readily, but structural isomerization which requires F-atom shift is absent. However, structural isomerization involving H-atom migration may occur, but, in the absence of deuterium labeling, cannot be observed.

The results on the MFE reaction are in accord with the earlier work of Trobridge and Jennings[4a] in that the zero-pressure extrapolated quantum yield of the decomposition is probably unity within experimental error and the lifetime of excited states involved is short (of the order of 10^{-10} sec). Because of the relatively small pressure effect and large error in the acetylene yield determination, the kinetic data of both studies are too scattered for precise mechanistic conclusions. Trobridge and Jennings found a linear pressure dependence for $\phi(C_2H_2)$ of the form $A-BP$, which is inconsistent with any simple, irreversible mechanism involving one or two excited intermediates. A similar, but even smaller, pressure dependence has been observed in the analogous reaction of vinyl chloride.[10]

For the DFE reactions, a simple one-excited-state mechanism

$$C_2H_2F_2 + Hg^* \longrightarrow C_2H_2F_2^* + Hg \qquad (1)$$

$$C_2H_2F_2^* \longrightarrow C_2HF + HF \qquad (2)$$

$$\xrightarrow{[M]} C_2H_2F_2 \qquad (3)$$

would predict the following kinetic equations

$$\phi(C_2HF)^{-1} = \phi^0(C_2HF) + (k_3/k_2)[M] \qquad (I)$$

$$[M]/2\phi(\text{isomer}) = (k_2/k_3) + [M] \qquad (II)$$

$$2\phi(\text{isomer})/\phi(C_2HF) = (k_3/k_2)[M] \qquad (III)$$

where ϕ^0 signifies the zero-pressure extrapolated quantum yield. The involvement of two excited intermediates

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(15) Equilibrium is reached only with $\ddot{C}{-}H$ and not with $\ddot{C}{-}F$ bond variations; spontaneous dissociation along the $R\ddot{C}{-}F$ coordinate leads to $R\ddot{C}^+ + F^-$. This tendency to overestimate the stability of ionic structures involving strongly polar bonds is a known defect of the EHMO method. It is found, however, that the heterolytic mode of cleavage is preferred even for the C–H bond, at least in the case of the $H{-}\ddot{C}CH_3$ linkage; the dissociation products of the process are the hydride ion and $CH_3C{:}^+$ carbonium ion.

$$C_2H_2F_2^* \longrightarrow C_2H_2F_2^{**} \quad (4)$$

$$\xrightarrow{[M]} C_2H_2F_2 \quad (5)$$

$$C_2H_2F_2^{**} \longrightarrow C_2HF + HF \quad (6)$$

$$\xrightarrow{[M]} C_2H_2F_2 \quad (7)$$

on the other hand, would lead to the relation

$$\frac{[1/\phi(C_2HF)] - 1}{[M]} = \left[\frac{k_5}{k_4} + \frac{k_7}{k_6}\right] + \frac{k_5k_7}{k_4k_6}[M] \quad (IV)$$

Assuming that the lifetimes of the two intermediates are approximately equal and that the collisional deactivation efficiencies are also equal, IV is reduced to

$$\phi(C_2HF)^{-1/2} = 1 + (k_5/k_4)[M] \quad (V)$$

All five relations were tested. Plots were prepared in two ways: (a) using the experimentally measured yields of monofluoroacetylene and (b) calculating the yields of monofluoroacetylene from the yields of the isomer, $\phi(C_2HF) = 1 - 2\phi(\text{isomer})$. The results are compiled in Table VII. Case b appears to give self-consistent results, indicating that the assumption that $\phi(C_2HF)^0$ equals unity is a plausible one. Both mechanisms (eq I and II as well as IV and V) obey linear relations, and it is not possible to determine whether this is due to scatter in the data or is a consequence of additional complexity in the mechanism.

Table VII. Evaluation of Kinetic Equations I–V

Eq	k_2, sec^{-1} × 10^{-9} Case a	 Case b
I	Curving	Linear
II	Linear; 2.6	
III	Linear; 1.2	Linear; 0.95
IV	Curving	Linear;[a] ~1
V	Curving	Linear;[a] 2.2

[a] $k_4 \sim k_6$.

The detailed path of decomposition is not well established even in the more extensively studied case of ethylene. From a thorough study of the triplet mercury photosensitized decomposition of *trans*-dideuterioethylene, Setser, Rabinovitch, and Placzek[3] have concluded that the second excited state is the ethylidene and that either this is the decomposition state or the formation of this state precedes the formation of the decomposition state.

A significant contribution to the ethylene reaction comes from the recent work of Cvetanović, Sato, and coworkers.[16] Using triplet cadmium atoms, benzene, toluene, isomeric xylenes, etc., as photosensitizers, these authors have shown that an activation energy of 25 kcal for the triplet ethylene → ethylidene isomerization and an excitation energy of 45 kcal for the lowest twisted triplet state of ethylene are consistent with the observed kinetic behavior of the systems they have investigated. This lends additional support to earlier contentions that the second excited state in the triplet photosensitization of ethylene is the ethylidene, as was first postulated by Callear and Cvetanović.[17] The triplet ground state of ethylidene has been estimated[18] to lie 69 kcal above ground state ethylene, and a recent semiempirical MO calculation[19] gave a value of 76 kcal for the energy barrier of the isomerization of ground state ethylene to ground state ethylidene.

As to the nature of the initial decomposition product, it has been tacitly implied in earlier discussions that the primary fragment is the acetylene structure. The possibility of vinylidene formation was intuitively considered unlikely on energetic grounds. Data concerning the stability of this species are lacking in the literature.

From the present MO calculations it is possible to derive semiquantitative numerical values for the energies of the vinylidene carbenes. Using the data in Tables IV and V, the energies of ground state $CH_2{=}C{:}$, $CHF{=}C{:}$, $CF_2{=}C{:}$, and $CHCl{=}C{:}$ are 95, 78, 44, and 110 kcal, respectively, above the corresponding ground state acetylene. The lowest excited states of these vinylidenes lie over *ca.* 1.5 eV above their ground states. By applying Hoffmann's empirical rule[14] that when the optimum σ^2 configuration has an EHMO energy less than 1.5 eV below the σp configuration at the same $>C{:}$ angle then the ground state is likely to be the triplet, it can be predicted that vinylidenes have a singlet σ^2 ground state. (In the present instance the limiting value appears to be 1.2 rather than 1.5 eV.) A concurrent, probably more reliable *ab initio* MO calculation on difluorovinylidene yielded a value of 36.4 kcal for the ground state energy above the ground state difluoroacetylene; for vinylidene, however, the *ab initio* value is considerably lower than the EHMO[20] value. Thus, we estimate ground state $CF_2{=}C{:}$, $CHF{=}C{:}$, and $CH{=}C{:}$ to lie about 40, 50, and 60 kcal above ground state acetylene.

Experimentally, the question of vinylidene *vs.* acetylene formation has been settled only for the triplet mercury sensitized decomposition of trifluoroethylene.[21] In this case it has been shown unequivocally that the primary decomposition product is the difluorovinylidene. Isomerization of this carbene to perfluoroacetylene appears to be slow because fluorine atom shift features an appreciable activation energy. The rearrangement of vinylidene or monofluorovinylidene to acetylene, however, is probably a very rapid process owing to the facility of hydrogen atom migration, and scavenging of these carbenes would be less feasible in practice.

Bond energy and thermochemical data concerning fluorocarbons are sparse and unreliable. To estimate the enthalpy changes of fluoroethylene decompositions we have to rely on the present computational results which indicate that both H_2 and HF eliminations become increasingly more difficult with increasing number of fluorine atoms in the molecule. We take the specific increment for both H_2 and HF detachment as +10 kcal per fluorine atom in the ethylene molecule. The results are given in Table VIII. According to

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(20) O. P. Strausz, R. J. Norstrom, H. E. Gunning, and I. G. Csizmadia, manuscript in preparation.

(21) O. P. Strausz, R. J. Norstrom, and H. E. Gunning, manuscript in preparation.

Table VIII. Estimated Enthalpy Changes in the Reactions of Ethylene and Haloethylenes

Products	H_2	HF	HCl
C_2H_2	41[a]	18[b]	24[a]
$CH_2{=}C{:}$	101	78	84
C_2HF	51	28	
$CFH{=}C{:}$	101	78	
C_2F_2	61	38	
$CF_2{=}C{:}$	101	78	

[a] S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **70**, 3336 (1966). [b] D. G. Moslov, *Khim. Tekhnol. Topl. Masel*, **3** (10), 50 (1958). The value of -69 kcal for $\Delta H_f{}^\circ$ of C_2HF reported in this article must be erroneous.

Table IX. Estimated State Energy Levels of Ethylenes and Ethylidenes[a]

	First excited state of				
	Ethylenes			Ethylidene	
	EHMO		Estimated skew triplet	EHMO	Estimated lowest triplet
	Vertical	Skew			
C_2H_4	118	84	45[b]	81	70[b]
$FHCCH_2$	122	93	50	64 ($H\ddot{C}CH_2F$)	56
				79 ($F\ddot{C}CH_3$)	99
FHCCHF (cis)	125	91	49	81 ($F\ddot{C}CH_2F$)	101
FHCCHF (trans)	125	88	47	78	98
F_2CCH_2	131	103	55	70 ($H\ddot{C}CHF_2$)	60
F_2CCFH	132	94	50	86 ($F\ddot{C}CHF_2$)	106
F_2CCF_2	135			60	80
$ClHCCH_2$	120	83	44	58 ($H\ddot{C}CH_2Cl$)	51
				77 ($Cl\ddot{C}CH_3$)	96

[a] Energy in kcal. [b] Taken from ref 16.

Table X. Estimated Rate Constants for Triplet Ethylene to Triplet Ethylidene Rearrangements[a]

Reaction	k, sec^{-1}	Reaction	k, sec^{-1}
$H_2C{=}CH_2 \rightarrow \ddot{C}HCH_3$	4.6×10^9	$CHF{=}CF_2 \rightarrow \ddot{C}FCHF_2$	1.2×10^6
$CHF{=}CH_2 \rightarrow \ddot{C}HCH_2F$	2.2×10^{10}	$CHF{=}CH_2 \rightarrow \ddot{C}FCH_3$	1.9×10^5
$CHCl{=}CH_2 \rightarrow \ddot{C}HCH_2Cl$	2.1×10^{10}	$CHCl{=}CH_2 \rightarrow \ddot{C}ClCH_3$	3.5×10^5
$CHF{=}CHF \rightarrow \ddot{C}FCH_2F$	8×10^7	$CF_2{=}CH_2 \rightarrow \ddot{C}HCHF_2$	1.8×10^{10}

[a] The unimolecular rate constants are based on an A factor of 1×10^{11} sec^{-1} for the ethylene reaction (ref 16) and are corrected for reaction path degeneracies. The number of effective oscillators used in the RRK formula was eight for ethylene,[16] with an increment of 1.5 added per halogen atom in the haloethylenes; *cf.* S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965); J. A. Kerr, A. W. Kirk, B. V. O'Grady, D. C. Phillips, and A. F. Trotman-Dickenson, *Discuss. Faraday Soc.*, **44**, 263 (1967).

this picture, vinylidene formation would be energetically feasible in the mercury photosensitization of not only trifluoroethylene, but all the partially fluorinated ethylenes, vinyl chloride, and ethylene as well. If, however, the reverse reaction, the insertion of vinylidene into HX, possesses an appreciable activation energy, all processes giving rise to vinylidenes *via* H_2 elimination would become too slow to be of significance.

We can now assess the activation energies and from these the relative rate constants for the isomerization reactions of triplet haloethylenes to ethylidenes, using our calculated EHMO excitation energies. These rate constants in turn will be compared to the experimental values.

The EHMO method does not take into account electron interactions and consequently provides only an average energy value of triplet and singlet states of a given spatial symmetry. These average values lie between those of the actual singlet and triplet states.[22]

In order to derive the energy of the lowest twisted triplet state of the ethylenes we assumed that the ratio E_T(actual) to E_{av}(calcd) is the same for all cases as for ethylene, that is, 45/84. This assumption may be permissible in view of the small variation of the calculated average energy with molecular structure (about $\pm 10\%$). A similar procedure was applied to the ethylidene carbenes. Here E_T(actual) was taken as 70 kcal and E_{av}(calcd) as 80.5 kcal. The relevant data are compiled in Table IX. It was also presumed that the $H\text{–}\ddot{C}\text{—}C\equiv$ type ethylidenes have a triplet ground state, while the $F\text{—}\ddot{C}\text{—}C\equiv$ type ethylidenes have a singlet ground state. This choice is based on accumulated experimental and theoretical evidence[14,23] as well as on our computational results, which show that the lowest excited states of $X\text{—}\ddot{C}\text{—}C\equiv$ type ethylidenes lie $\geqslant 1.2$ eV above the ground state. The lowest excited triplet state in these cases was taken to be 20 kcal above the singlet ground state; *cf.* Table V. (In CF_2 the lowest excited triplet has been estimated to lie $\sim$45 kcal above the ground state singlet.[9])

The rate constants for the triplet ethylene to ethylidene rearrangement can now be calculated by the RRK formula

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(22) *Cf.* L. C. Cusachs and J. H. Corrington in "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. Wiberg, Ed., Yale University Press, New Haven, Conn., 1969, pointed out that the formula for the singlet ($^1\Delta E$) and triplet ($^3\Delta E$) excitation energy values is simpler in the LCAO-MO method than in the SCF-MO formalism. Accordingly, $^1\Delta E = \epsilon_a - \epsilon_b + K_{ab}$ and $^3\Delta E = \epsilon_a - \epsilon_b - K_{ab}$, where ϵ_a and ϵ_b are the MO energy levels of the two orbitals involved in the excitation ($\epsilon_b \rightarrow \epsilon_a$) and K_{ab} is the two-electron exchange integral. Consequently, the arithmetical mean of these two equations predicts the MO energy differences to be inbetween the singlet and triplet excitation energies; *i.e.*, $(^1\Delta E + {}^3\Delta E)/2 = \epsilon_a - \epsilon_b$.

(23) J. Duchesne and L. Burnelle, *J. Chem. Phys.*, **21**, 2005 (1953); C. W. Mathews, *ibid.*, **45**, 1068 (1966); A. J. Merer and D. N. Travish, *Can. J. Phys.*, **44**, 525 and 1541 (1966); E. Wasserman, L. Barash, and W. A. Yager, *J. Amer. Chem. Soc.*, **87**, 4974 (1965).

$$k = A\left(1 - \frac{E_a}{115 - E_T(\text{ethylene})}\right)^{s-1}$$

where E_a is the energy difference between triplet ethylidene and triplet twisted ethylene if the preexponential factors are taken to be constants. The data are given in Table X.

For monohalogenated ethylenes, hydrogen migration may occur in two different directions, giving two distinctly different ethylidenes. If, in the course of reaction, the spin is maintained, as is likely, hydrogen migration toward the halogen-containing carbon atom will be several orders of magnitude faster than migration in the opposite direction. Consequently, the intervention of only those types of ethylidenes which have a hydrogen atom on the carbene carbon, and therefore possess a triplet ground state, can be anticipated in the reaction.

For vinyl chloride, MFE, and 1,1-DFE, the calculated rate constants of isomerization are equal or somewhat larger than for ethylene, and the trend is consistent with experimental results, which for comparison are tabulated in Table XI. For 1,2-DFE and TFE, however, which by hydrogen migration can form only excited triplet ethylidenes, the estimated rate constants of isomerization are significantly lower than for ethylene or than those measured for their overall decomposition. This suggests that ethylidenes are not intermediates in the triplet state decompositions of these ethylenes.

Table XI. Experimental Rate Constants for the Ethylene and Haloethylene Reactions

Olefin	$k \times 10^{-9}$, sec^{-1} Ethylene → ethylidene	 Decomposition
C_2H_4	1.8,[a] 3.5[b]	0.37[b]
C_2H_3F		~7[c]
$C_2H_2F_2$	~1	~1
C_2H_3Cl		10[d]
C_2HF_3		0.2[e]

[a] Reference 6. [b] Reference 2. [c] Reference 3. [d] Reference 10. [e] Reference 21.

Thus, the present results support the contention that the ethylidenes, when formed, are intermediates in the decomposition sequence. It is, however, not possible to determine whether molecular detachment occurs from the ethylidene state or from a state which forms subsequently to ethylidene. All the ethylidenes possess a substantial excess of vibrational energy. Their decomposition into acetylene and HX is a spin-forbidden but exothermic process, having a relatively large activation energy. By proper choice of Arrhenius parameters, it can be shown that decomposition rate constants consistent with the experimental values can be obtained. Thus, taking a normal frequency factor of 10^{13} and activation energies of 35 and 32 kcal, respectively, for H_2 and HF or HCl detachment, the following rate constants are computed: C_2H_4, 2.5×10^8; C_2H_3F, 1.4×10^{10}; C_2H_3Cl, 2.7×10^{10}; CH_2CF_2, 1.7×10^9 sec^{-1}. These compare favorably with the experimental values listed in Table XI. Naturally, the same rate constant values could be obtained by taking proportionally lower frequency factors and activation energies. The activation energy of the ethylidene reaction, however, cannot be lower than ~20 kcal because, in the triplet Cd-atom sensitization of ethylene (available total excitation energy is about 90 kcal), decomposition is only a very minor reaction if it occurs at all.

If the decomposition state is indeed the ethylidene, the isomerization reactions, triplet ethylene → triplet ethylidene (forward) → triplet ethylene (reverse) should occur several times prior to decomposition because the rate constant of the reverse reaction, k_r, should be of the same order of magnitude or larger than the decomposition rate constant.[24]

For the C_2H_4, C_2H_3F, C_2H_3Cl, and 1,1-$C_2H_2F_2$ decompositions, the acetylene must be the primary product for energetic or structural reasons. For the decomposition of C_2HF_3, the primary product is the difluorovinylidene, and the kinetic data favor monofluorovinylidene as the primary decomposition product of the 1,2-$C_2H_2F_2$ reaction, The monofluorovinylidene could subsequently readily isomerize to the observed product, monofluoroacetylene. It can be shown by MO calculations[20] that hydrogen atom migration in vinylidene has a much lower activation energy than fluorine atom migration, and the lifetime of monofluorovinylidene would be expected to be much shorter than that of difluorovinylidene with respect to unimolecular isomerization to acetylene.

The vinylidenes in the C_2HF_3 and 1,2-$C_2H_2F_2$ reactions may be envisaged as originating either directly from the triplet ethylene, or, after intersystem crossing, from the vibrationally excited ground state ethylene. (The intersystem crossing may be facilitated by heavy atom preturbation due to the presence of fluorine atoms.) It appears unlikely that the vinylidenes would come from the ethylidenes.

Assuming that the decomposition state of the TFE and 1,2-DFE reaction is the vibrationally excited ground state ethylene, the experimental rate constants can be shown to be reproducible by reasonable choices for the Arrhenius parameters. If the activation energy is taken to be equal to the estimated endothermicity of the reaction and the frequency factor, 1.85×10^{14} sec^{-1}, recently reported[25] for the unimolecular, geminal elimination of HF from chemically activated CHF_2CD_3 is used, one obtains, after correcting for reaction path degeneracy (k's in sec^{-1})

$$k_{\text{TFE}} = 0.93 \times 10^{14}(1 - 78/115)^{11.5} = 2.7 \times 10^8$$

$$k_{1,1\text{-DFE}} = 1.85 \times 10^{14}(1 - 78/115)^{10} = 2.8 \times 10^9$$

in approximate agreement with experiment. This is admittedly not a sensitive and reliable test; nonetheless, when taken in conjunction with earlier conclusions, it appears to justify some confidence.

Thus it would seem that, in those cases where ethylidene is an intermediate of the decomposition sequence, the primary product of the reaction is the acetylene,

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(24) The value of k_r is largely determined by the frequency factor since, even if there is a small energy barrier for the reaction, the excess vibrational energy in the molecule is so large (~45–50 kcal) that the energy term in the RRK formula would not be much less than ~0.1. The frequency factor for the forward reaction[16] is ~1×10^{11} sec^{-1} ($\Delta S^{\ddagger}$ ~ −12 eu) and for the reverse reaction it cannot be lower than 10^9–10^{10} sec^{-1}. Therefore k_r cannot be lower than ~10^8 sec^{-1}. If this is the case, it also follows that the experimental rate constant values for decomposition and ethylidene formation are lower than the actual values, since in none of the kinetic treatments has the reverse of ethylidene formation been included.

(25) M. J. Perona, J. T. Bryant, and G. O. Pritchard, *J. Amer. Chem. Soc.*, **90**, 4782 (1968).

which could structurally readily form from ethylidene. In those cases where ethylidene is not an intermediate of the decomposition sequence, the primary reaction product is the vinylidene, which can structurally arise only from the ethylene.

There is no clear-cut experimental evidence against the possibility of ethylidene being the decomposition state in the triplet mercury sensitization of ethylene.[26]

If, on the other hand, the decomposition state is not the ethylidene but the vibrationally excited singlet ground state of ethylene, it is difficult to rationalize why the intersystem crossing, triplet ethylidene → singlet ethylidene, should be so efficient in a light molecule such as ethylene. The rate constant of this reaction should be $\gg 3.7 \times 10^8$ sec^{-1} in order not to become a rate-controlling kinetic factor. From the present MO calculations the lowest excited singlet state of ethylidene appears to lie at least 10 kcal above the triplet ground state, and thus the intersystem crossing would be a considerably uphill process.

In this connection it may be pointed out that, in low-energy triplet photosensitization of ethylene, it has been noted[16] that the isomerization of triplet ethylene to ethylidene is incomplete even though the excitation energy available exceeds the minimum value of 69 kcal required for this reaction. To explain the lack of complete isomerization, another competing transition from the triplet ethylene state has been invoked. It appears that this transition is the intersystem crossing to the ground state of ethylene. The process should have an activation energy of the order of 7 kcal. On these premises, one can estimate, from the experimental data reported in ref 16, the frequency factor of the transition, which would be of the order of 10^7 sec^{-1}. This appears to be the right order of magnitude for an intersystem crossing in a small molecule and it is about a factor of 10^4 lower than the value required for the triplet ethylidene → singlet ethylidene intersystem crossing discussed above.

In conclusion, it should be stressed that the model developed in this article for the triplet mercury photosensitization of haloethylenes, while being capable of accounting for the basic kinetic features of the reactions in a self-consistent and plausible manner, is not considered as a proof of the mechanism. Rather, it is suggested as a working hypothesis, which should be subjected to further tests of experiment.

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(26) The few existing pieces of information which seem to militate against it are the kinetic computational results of Hampson and McNesby,[4b] the result of Kibby and Kistiakowsky [C. L. Kibby and G. B. Kistiakowsky, *J. Phys. Chem.*, 70, 126 (1966)] on the photolysis of deuterium-labeled diazoethane, and the fact that no addition product from the reaction of triplet ethylidene to ethylene has been detected: J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 3718 (1963).

Hampson and McNesby have shown by an approximate application of the theory of unimolecular reactions that the rate constant for decomposition of ethylene excited by triplet mercury atoms falls into the proper sequence when compared to decomposition of excited ethylenes having differing energy contents. This, however, does not prove the mechanism since, as was pointed out above, agreement with all experimental data can be achieved by proper choice of the Arrhenius parameters for the hypothetical ethylidene decomposition reaction as well.

Kibby and Kistiakowsky determined the isotopic distribution of the hydrogen product from the photolysis of CD_3CHN_2. The primary photolytic step here involves the loss of N_2, giving rise to a presumably singlet, excited ethylidene. Molecular hydrogen detachment from the initial ethylidene should give only D_2, while decomposition from the ethylene state gives HD as well. Experimentally both D_2 and HD were observed in a ratio of 1.00 to 1.21. This result still may be consistent with ethylidene decomposition since ethylidene → ethylene → ethylidene rearrangement may be competing with decomposition.

The failure to obtain methylcyclopropane, the expected addition product of ethylidene to ethylene, in triplet photosensitization may simply be due to the low relative efficiency of this reaction. The addition reactions of triplet divalent species to monoolefins possess a small activation energy and a steric factor of 0.1 or less. Assuming a plausible value of $\sim$4 kcal for the activation energy, at 1 atm pressure of ethylene (where the excited triplet ethylene intermediate would already be largely quenched) the addition reaction would be two to three orders of magnitude slower than the competing reactions. [Addition of ethylidene to propylene has been observed in the 4358-Å gas-phase photolysis of diazoethane in the presence of propylene; *cf.* H. M. Frey, *J. Chem. Soc.*, 2293 (1962). More recently, addition of ethylidene to ethylene has been shown to occur in the low-temperature solid-phase photolysis of ethylene at 1470 Å; *cf.* E. Tschuikow-Roux, J. R. McNesby, W. M. Jackson, and J. L. Faris, *J. Phys. Chem.*, **71**, 1531 (1967)].