tion of the carbanion ($X = C^-$; $Y = N$) facilitates the closing of vinylazides to the anions of *V*-triazole, while guanylazide hydrochloride (**4a**) ($X = N^+H_2$; $Y = N$; $R = NH_2$) is stable contrary to the case for guanylazide itself.

Finally, one can say qualitatively that the activation energy for the process I → IV is due essentially to the bending of angle γ (N_3-N_4-N_5) while that for the process IX → IV is due to the rupture of the bond σ_{15} and to the loss of the delocalization energy in tetrazole.

References and Notes

(1) (a) Laboratoire de Chimie Quantique, Université Catholique de Louvain; (b) Département de Chimie Organique, Université d'Aix-Marseille.
(2) R. M. Claramunt, J. Elguero, and A. J. H. Summers, *Adv. Heterocycl. Chem.*, in preparation.
(3) (a) E. Alcalde, J. de Mendoza, and J. Elguero, *J. Chem. Soc., Chem. Commun.*, 411 (1974); (b) *J. Heterocycl. Chem.*, **11**, 921 (1974); (c) R. Faure, J. P. Galy, G. Giusti, and E. J. Vincent, *Org. Magn. Reson.*, **6**, 485 (1974); (d) E. Alcalde and R. M. Claramunt, *Tetrahedron Lett.*, 1523 (1975).
(4) (a) R. Faure, E. J. Vincent, and J. Elguero, *Tetrahedron Lett.*, 2703 (1973); (b) R. Faure, E. J. Vincent, R. M. Claramunt, J. M. Fabrega, and J. Elguero, *Tetrahedron*, submitted for publication.
(5) R. Faure, unpublished results.
(6) R. N. Butler, *Chem. Ind.* (*London*), 371 (1973).
(7) M. Tisler, *Synthesis*, 123 (1973).
(8) J. Elguero, *Bull. Soc. Chim. Fr.*, 1925 (1971).
(9) H. Reimlinger, *Chem. Ber.*, **103**, 1900 (1970).
(10) H. de Suray, G. Leroy, and J. Weiler, *Tetrahedron Lett.*, 2209 (1974).
(11) G. Leroy and M. Sana, *Tetrahedron*, to be submitted for publication.
(12) G. L'abbé and G. Mathijs, *J. Org. Chem.*, **39**, 1778 (1974).
(13) G. Smolinsky and C. A. Pride, "The Chemistry of Azido Group", S. Patai, Ed., Interscience, New York, N.Y., 1971, p 555.
(14) G. Tennant and R. J. S. Vevers, *J. Chem. Soc., Chem. Commun.*, 671 (1974).
(15) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
(16) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(17) (a) M. D. Newton, W. A. Lathan, and W. J. Hehre, *J. Chem. Phys.*, **52**, 4064 (1970); (b) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).
(18) E. Clementi, M. Clementi, and D. R. Davis, *J. Chem. Phys.*, **46**, 4725 (1967).
(19) S. J. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960).
(20) P. Dominiano and A. Musatti, *Cryst. Struct. Commun.*, **3**, 713 (1974].
(21) H. Henke, H. Bärnighausen, *Acta Crystallogr., Sect. B*, **28**, 1100 (1972).
(22) P. Dominiano and A. Musatti, *Cryst. Struct. Commun.*, **3**, 335 (1974).
(23) K. Britts and I. L. Karle, *Acta Crystallogr.*, **22**, 308 (1967).
(24) M. Roche and L. Pujol, *Bull. Soc. Chim. Fr.*, **4**, 1088 (1969).
(25) W. D. Krugh and L. P. Gold, *J. Mol. Spectrosc.*, **49**, 423 (1974).
(26) R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Am. Chem. Soc.*, **77**, 2264 (1955).
(27) G. Leroy and M. Sana, to be submitted for publication.
(28) L. F. Avramenko, V. Ya. Pochinok, and Yu. S. Rozum, *J. Gen. Chem. USSR* (*Engl. Transl.*), **33**, 968 (1963).
(29) G. A. Reynolds, J. A. Van Allan, and J. F. Tinker, *J. Org. Chem.*, **24**, 1205 (1959).

The Mercury 6($^3P_1$), Cadmium 5($^3P_1$), and Benzene ($^3B_{1u}$) Photosensitization of Vinyl Fluoride

S. Tsunashima, H. E. Gunning, and O. P. Strausz*

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

Received July 11, 1975

Abstract: Triplet state vinyl fluoride molecules containing different amounts of excess vibrational energies were produced by energy transfer from Hg ($^3P_1$) atoms at 27 °C, Cd ($^3P_1$) atoms at 275 °C, and benzene ($^3B_{1u}$) molecules at 27 °C. In all three systems vinyl fluoride was found to undergo unimolecular decomposition to yield acetylene and hydrogen fluoride with a zero pressure extrapolated quantum yield of approximately unity in the metal atom sensitized systems, and 0.31 in the benzene-sensitized system. The decomposition sequence involves at least two different excited intermediates, the (π,π*) triplet ethylene and probably its isomeric triplet 2-fluoroethylidene. From the rate constant values determined ($k(\text{Hg}) = 3.8 \times 10^{10}$ s^{-1} (27 °C), $k(\text{Cd}) = 8.3 \times 10^8$ s^{-1} (275 °C), and $k(C_6H_6) = 4.6 \times 10^8$ s^{-1} (27 °C)) the following values were derived for the Arrhenius parameters of the decomposition reaction, $^3(\ddot{C}H{-}CH_2F) \rightarrow C_2H_2 + HF$, $A = (2.1 \pm 1.0) \times 10^{12}$ s^{-1} and $E_a = 22.4 \pm 1.7$ kcal/mol. The Arrhenius parameters for the $^3(CH_2CHF) \rightarrow {}^3(\ddot{C}H{-}CH_2F)$ rearrangement were estimated to have the values: $A = 9 \times 10^{10}$ s^{-1} and $E_a = 6.0$ kcal/mol.

Earlier studies[1,2] of the mercury 6($^3P_1$) photosensitized decomposition of vinyl fluoride at room temperature have shown that triplet excited vinyl fluoride molecules decompose exclusively to acetylene and hydrogen fluoride and that hydrogen elimination does not occur. The reaction follows an excited state mechanism involving one or more reactive intermediates. Because of the lack of sufficient accuracy in the kinetic data due to the small effect of pressure on the decomposition, it was not possible to establish the number of intermediates involved. The observed linear pressure dependence for the quantum yield of acetylene formation, $\phi(C_2H_2) = A - B[C_2H_3F]$, is inconsistent with any plausible mechanism. The decomposition rate constant for vinyl fluoride and vinyl chloride[3] was an order of magnitude higher than that for ethylene.[4-6] The shorter lifetime of the reaction intermediates and higher rate constant for the decomposition reaction was attributed to the lower energy of the triplet ethylidene state and the more favorable energetics of the hydrogen halide elimination step: $C_2H_4 \rightarrow C_2H_2 + H_2$, $\Delta H = 41.7$ kcal/mol; $C_2H_3F \rightarrow C_2H_2 + HF$, $\Delta H = 18$ kcal/mol.

The mercury ($^3P_1$) photosensitized decomposition of the three isomeric difluoroethylenes, *cis*-CHFCHF, *trans*-CHFCHF, and CH_2CF_2, has also been investigated.[2] These reactions are somewhat slower and even though it was possible to obtain reproducible and reasonably accurate kinetic data, they appeared to satisfy equally well a one excited state and a two excited state mechanism. Furthermore, while the experimental decomposition kinetics of the three isomeric molecules were identical, the 1,1 and 1,2 isomers were postulated to follow different decomposition paths, the former involving a triplet ethylidene intermediate:

$$CF_2CH_2 + Hg^* \rightarrow CF_2CH_2^* + Hg$$

$$CF_2CH_2^* \rightarrow CF_2H\ddot{C}H^*$$

$$CF_2H\ddot{C}H^* \rightarrow CF{\equiv}CH + HF$$

and the latter not involving such species:

$$\mathrm{CFHCFH + Hg^* \rightarrow CFHCFH^* + Hg}$$

$$\mathrm{CFHCFH^* \rightarrow CFH{=}C{:} + HF}$$

Only the decomposition sequences of vinyl fluoride and 1,1-difluoroethylene are believed to involve ethylidene intermediates since the ground state of these carbenes is a triplet.[2,7] Decomposition of the vibrationally excited triplet ethylidenes gives monofluoroacetylene and hydrogen fluoride, while decomposition of the triplet ethylene probably gives singlet ground state monofluorovinylidene.

Other low-energy triplet sensitizers such as cadmium atoms, benzene, toluene, xylenes, etc., have also been employed in the study of the reactions of triplet ethylene.[8-11] With these sensitizers isomerization is facile, but decomposition is negligibly slow because of the insufficient excitation energy present.

In order to elucidate additional details of the mechanism in the decomposition of triplet state vinyl fluoride, the reaction has been reinvestigated using three different triplet sensitizers, Hg ($^3P_1$) atoms, Cd ($^3P_1$) atoms, and benzene ($^3B_{1u}$) molecules with excitation energies of 112.7, 87.7, and 84.4 kcal/mol, respectively.

Experimental Section

The apparatus used was similar to those described in ref 2, 3, and 10. In the mercury sensitization experiments, the reaction cell was a 2 × 10 cm cylindrical Pyrex vessel with quartz windows. The light source was a mercury low-pressure resonance lamp (Hanovia No. 687A45), equipped with a Vycor 791 filter. Absorbed light intensities were determined by propane actinometry.[12]

The measured quantum yields of acetylene were corrected for the variation in absorbed light intensity with vinyl fluoride pressure caused by the pressure broadening of the mercury resonance line using the function[2] $1/f = 1.00 + 2.69/P$, where f is the fraction of incident light intensity absorbed and P is the substrate pressure in Torr.

In the cadmium-sensitization experiments three different cylindrical quartz reaction vessels with dimensions of 5 × 2, 5 × 5, and 5 × 10 cm were used. They were equipped with a side arm containing cadmium. The temperatures of the cell and the side arm were regulated by electric furnaces and kept at 275 ± 1° and 270 ± 1 °C, respectively. The light source was a discharge lamp containing a few pieces of cadmium and 2 Torr of argon and was equipped with a Pyrex filter to eliminate the 228.8-nm resonance line. The absorbed light intensity at 326.1 nm was determined from the Cd ($^3P_1$) + *cis*-2-butene (20 Torr) system assuming $\phi_{trans\text{-}2\text{-butene}} = 0.5$.[13,14]

Transmitted light intensities were monitored by a Phillips 92 AV photocell, operated by a Stark Power supply (Model PS 501) mounted behind the cell. The emerging beam was roughly collimated by means of a 1.0 cm i.d. × 10 cm long blackened tube. In the cadmium-sensitization experiments a 313.0-nm interference filter was interposed between the cell and the photocell. The photocurrent was measured by a picoammeter (Keithly Instruments 410 A) and/or recorded on a Hewlett Packard 7101 B strip chart recorder.

In the benzene-sensitization experiments a mercury free vacuum line was used. The reaction mixtures were prepared in calibrated volumes and the pressures were read on a Wallace-Tierman dial manometer. After equilibration, the irradiations were carried out in a 5 × 5 cylindrical reaction vessel through a Vycor 791 filter. The low-pressure mercury arc was used. At the conclusion of irradiation the volatile reaction products were separated from the benzene by low-temperature distillation at −107 °C (2,2,4-trimethylpentane slush). The absorbed light intensities were determined using *cis*-2-butene actinometry.[15-19] Since conversions were high the initial rate of *trans*-2-butene formation was calculated from the equation:

$$R_{trans\text{-}C_4H_8} = \frac{[cis\text{-}C_4H_8] + [trans\text{-}C_4H_8]}{2t} \ln \frac{[cis\text{-}C_4H_8] + [trans\text{-}C_4H_8]}{[cis\text{-}C_4H_8] - [trans\text{-}C_4H_8]}$$

where t is the exposure time.

Table I. Quantum Yields of Acetylene Formation as a Function of Pressure from the Hg ($^3P_1$)^a and Cd ($^3P_1$)^b Sensitization of Vinyl Fluoride

Hg ($^3P_1$)			Cd ($^3P_1$)		
$P(C_2H_3F)$, Torr	$1/f^c$	$\phi(C_2H_2)_{corr}$	$P(C_2H_3F)$, Torr	Cell^d	$\phi(C_2H_2)$
8.8	1.303	0.962	7.8	i	0.739
13.2	1.202	0.930	9.8	i	0.743
19.8	1.135	0.910	11.2	i	0.692
24.4	1.109	0.966	11.3	ii	0.717
29.0	1.092	0.935	14.2	i	0.719
29.3	1.091	0.967	15.9	ii	0.785
42.2	1.063	0.962	16.4	i	0.660
45.5	1.059	0.938	18.6	ii	0.725
51.7	1.052	0.934	20.0	i	0.636
74.6	1.036	0.914	21.2	ii	0.667
106	1.025	0.933	22.4	ii	0.661
168	1.016	0.931	25.0	i	0.600
211	1.013	0.917	27.7	ii	0.682
240	1.011	0.898	34.0	ii	0.542
320	1.008	0.787	34.6	i	0.584
438	1.006	0.714	35.9	ii	0.608
515	1.005	0.670	40.0	ii	0.617
646	1.004	0.600	51.2	ii	0.452
			51.6	ii	0.550
			56.8	ii	0.549
			70.2	i	0.515
			75.2	ii	0.532
			95.4	ii	0.349
			98.0	ii	0.464
			101.6	i	0.490
			127.0	ii	0.421
			147.6	ii	0.327
			202.2	ii	0.256
			247.8	ii	0.240
			295.0	iii	0.220
			321.4	ii	0.184
			357.8	iii	0.170
			395.8	ii	0.162
			430.4	ii	0.139
			494.6	ii	0.129
			510.2	ii	0.109
			666.4	ii	0.094

[a] At 27 °C. [b] At 275 °C. [c] Pressure broadening correction factor: $1/f = 1.00 + 2.67/P$. [d] Cell length: (i) = 5.0 cm, (ii) = 2.0 cm, and (iii) = 10.0 cm.

Materials. Vinyl fluoride and propane (Matheson) were purified by trap-to-trap distillation in vacuo. *cis*-2-Butene (Matheson) was purified by GC on a 28-ft dibutyl maleate column at 25 °C. Cadmium (Alfa Inorganic, 99.9999%) was used as such. Reagent grade benzene (McArthur) was purified by sulfuric acid treatment, distillation, and crystallization at 0 °C.

Analysis. Reaction mixtures were analyzed by GC on a 1-m Porapak N column at room temperature. In experiments conducted at high pressures, the reaction mixture was analyzed in several separate fractions. Hydrogen fluoride could not be measured.

Results

Mercury Photosensitization. As found previously[1,2] the only retrievable product in the room temperature reaction is acetylene the quantum yield of which was measured as a function of substrate pressure in the range of 9 to 646 Torr. The experimental values were corrected for pressure broadening and are presented in Table I. Extrapolation to zero pressure of C_2H_3F gives a value of approximately unity for acetylene formation and, by inference, for C_2H_3F disappearance.

Cadmium Photosensitization. Quantum yields for the only detectable product, acetylene, were measured as a function of C_2H_3F pressure at 275 °C in the range of 8 to 666 Torr. The results are also presented in Table I. The thermal stability of vinyl fluoride at the reaction tempera-

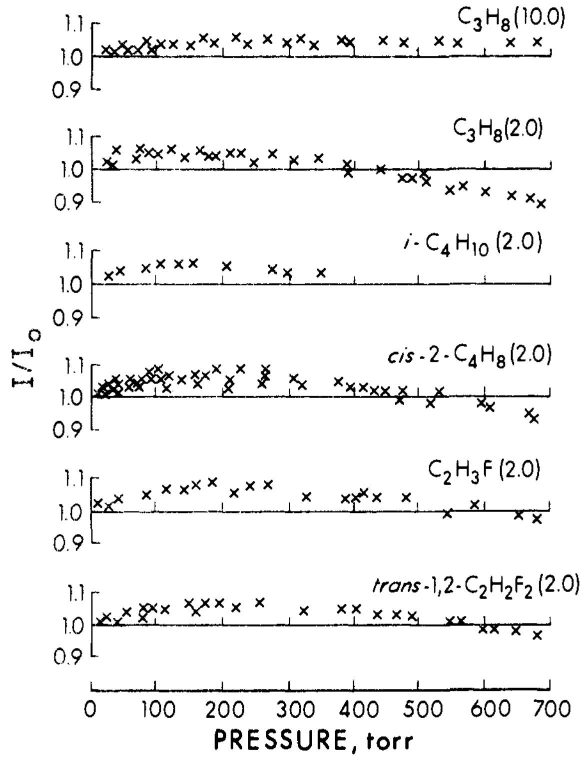


Figure 1. The effect of C_3H_8, *i*-C_4H_{10}, *cis*-2-C_4H_8, C_2H_3F, and *trans*-1,2-$C_2H_2F_2$ pressure on the absorption of the 326.1-nm resonance line of cadmium at 275 °C. The figures in brackets indicate the absorption path in centimeters.

ture was checked and no significant decomposition was found to occur during the time of photolyses. As in the mercury case, the extrapolated quantum yield at zero pressure is unity.

The effect of pressure broadening on the apparent quantum yields was examined in an auxiliary study using a 10 cm and a 2 cm long photolysis cell. From the data plotted in Figure 1 for vinyl fluoride and some other quenchers it is seen that the effect is small, even in the 2 cm long cell, and was not taken into consideration in the kinetic treatment of the reaction. It should be mentioned that no previous data have appeared in the literature on pressure broadening effects in cadmium photosensitization.

In the evaluation of data it is assumed that the excited intermediates involved in the reaction are quenched with unit collision efficiency by vinyl fluoride. In order to check on the validity of this assumption the quenching efficiency of another olefin, *cis*-2-butene, relative to vinyl fluoride, was also determined. Using 20 Torr of C_2H_3F the quantum yields of acetylene formation from vinyl fluoride and of *trans*-2-butene formation from *cis*-2-butene were measured as a function of the pressure of added *cis*-2-butene. The results are given in Table II.

Benzene Photosensitization. In addition to acetylene, three isomeric adducts of the empirical formula $C_2H_3F \cdot C_6H_6$ were detected in small yields in the room-temperature reaction, but only the rate of acetylene formation was measured quantitatively. From the data presented in Table III it is seen that at a constant pressure of C_2H_3F of 10 Torr, the yield of acetylene increases with increasing benzene pressure up to ca. 15 Torr after which the acetylene yield starts to decline. The rising trend is due to the increase in light absorption by benzene and the decline to the deactivating effect of benzene on the excited C_2H_3F molecules. The effect of C_2H_3F pressure on the acetylene yield at a constant benzene pressure of 10 Torr is seen from the results given in Table IV. The suppressing effect of pressure is evidently more pronounced here than in the higher energy mercury or cadmium sensitized systems. Curiously, a slow decomposition was found to take place in the absence of benzene, the rate of which, however, was negligibly slow as compared to the benzene-photosensitized reaction. It was probably due to photosensitization by trace quantities of benzene or mercury present in the line.

Table II. Quantum Yields of Acetylene and *trans*-2-Butene Formation as a Function of *cis*-2-Butene Pressure from the Cd ($^3P_1$) Sensitization of Vinyl Fluoride in the Presence of *cis*-2-Butene[a]

	Quantum yields	
P(*cis*-2-C_4H_8), Torr	Acetylene	*trans*-2-Butene
0	0.632	0
3.60	0.451	0.092
4.98	0.455	0.124
9.76	0.336	0.191
15.1	0.274	0.235
20.0	0.229	0.273
29.7	0.161	0.332
39.4	0.134	0.366

[a] $P(C_2H_3F)$ = 20 Torr; T = 275 °C.

Table III. Rate of Acetylene Formation from the Benzene ($^3B_{1u}$) Sensitization of Vinyl Fluoride as a Function of Benzene Pressure[a]

$P(C_6H_6)$, Torr	$R(C_2H_2)$, μmol/(cm^3 min)	$P(C_6H_6)$, Torr	$R(C_2H_2)$, μmol/(cm^3 min)
2.0	8.01×10^{-4}	10.0	1.99×10^{-3}
3.0	1.63×10^{-3}	15.0	2.44×10^{-3}
5.0	1.61×10^{-3}	20.0	2.06×10^{-3}
7.5	2.11×10^{-3}		

[a] $P(C_2H_3F)$ = 10.0 ± 0.1 Torr; T = 27 °C.

Table IV. Rate of Acetylene Formation from the Benzene ($^3B_{1u}$) Sensitization of Vinyl Fluoride as a Function of Vinyl Fluoride Pressure[a]

$P(C_2H_3F)$, Torr	Time, min	$\phi(C_2H_2)'$	A	$1/\phi(C_2H_2)'A$
5.02	3	0.373	1.028	2.609
10.0	5	0.350	1.054	2.711
15.0	7	0.298	1.082	3.102
20.0	15	0.275	1.108	3.282
29.7	15	0.221	1.158	3.906
39.9	30	0.196	1.213	4.206
56.1	40	0.181	1.302	4.243
80.0	70	0.123	1.433	5.673
100	90	0.103	1.532	6.338
120	100	0.0820	1.646	7.411
140	140	0.0693	1.753	8.230
171	150	0.0646	1.919	8.066
193	150	0.0704	2.041	6.960
232	150	0.0417	2.251	10.652
10.0[b]	35	0.56×10^{-2}		
20.0[b]	40	0.71×10^{-2}		
51.5[b]	45	0.41×10^{-2}		

[a] T = 27 °C. $P(C_6H_6)$ = 10 Torr. [b] $P(C_6H_6)$ = 0.

Finally, the relative quenching efficiencies of C_2H_3F and *cis*-2-butene toward triplet benzene, and those of C_2H_3F and benzene toward triplet C_2H_3F, were determined using a fixed pressure, 10 Torr each of benzene and *cis*-butene and varying the pressure of C_2H_3F. The data are tabulated in Table V.

Discussion

The steady-state treatment of a simple one excited state mechanism

$$S^* + C_2H_3F \rightarrow S + C_2H_3F^* \quad (1)$$

$$C_2H_3F^* \rightarrow C_2H_2 + HF \quad (2)$$

$$C_2H_3F^* + C_2H_3F \rightarrow 2C_2H_3F \quad (3)$$

where S* is the sensitizer, leads to the kinetic equation

$$\phi(C_2H_2)^{-1} = 1 + (k_3/k_2)[C_2H_3F] \quad (I)$$

A two excited state mechanism, which has been considered for the triplet state decomposition of ethylene and 1,1-difluoroethylene, consists of steps 1-6,

$$C_2H_3F^* \rightarrow C_2H_3F^{**} \quad (4)$$

$$C_2H_3F^{**} \rightarrow C_2H_2 + HF \quad (5)$$

$$C_2H_3F^{**} + C_2H_3F \rightarrow 2C_2H_3F \quad (6)$$

and leads to a pressure dependence of the quantum yield of acetylene formation of the form

$$\frac{\phi(C_2H_2)^{-1} - 1}{[C_2H_3F]} = \left(\frac{k_3}{k_4} + \frac{k_6}{k_5}\right) + \left(\frac{k_3k_6}{k_4k_5}\right)[C_2H_3F] \quad (II)$$

Equations I and II were tested for all three systems studied. The cadmium- and benzene-sensitized systems (the latter with appropriate modification to correct for quenching of the ($^1B_{2u}$) state of benzene (vide infra)) appear to obey eq I, Figures 2 and 3, and the mercury-sensitized system, a simplified form of eq II. In the latter system, because of the relatively small effect of pressure on the reaction, and the large errors associated with measuring small quantities of acetylene in the presence of a large excess of vinyl fluoride, eq II is extremely sensitive to experimental error.

If it is assumed that $k_3/k_4 \sim k_6/k_5$ then eq II reduces to

$$\phi(C_2H_2)^{-1/2} = 1 + (k_6/k_5)[C_2H_3F] \quad (III)$$

which is less sensitive to experimental error. A plot of the experimental results for the mercury-sensitized system, shown in Figure 4, indicates that this system obeys eq III.

Thus, we conclude that in the mercury-sensitized system there are two excited intermediates, while in the cadmium- and benzene-sensitized systems there is apparently only one excited intermediate involved. If, however, the latter systems follow a two excited state mechanism with widely different values for k_4 and k_5, the overall rate-controlling step will be the slower process yielding apparent one excited state kinetics.

To calculate the values of k_4 and k_5 we adopt the customary assumption that the collisional deactivation steps proceed with gas kinetic collision efficiency. Taking $k_3 = k_6 = 3.0 \times 10^{11}$ l. mol^{-1} s^{-1} at room temperature, corresponding to a collision cross section of ~30 Å^2, the values of the rate constants calculated from the slopes of Figures 2-4 are:

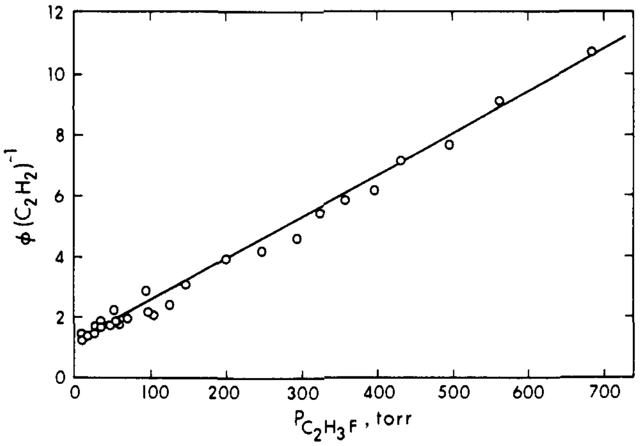


Figure 2. Plot of $\phi(C_2H_2)^{-1}$ vs. C_2H_3F pressure in the Cd ($^3P_1$) sensitized decomposition of C_2H_3F. Temperature: 275 °C.

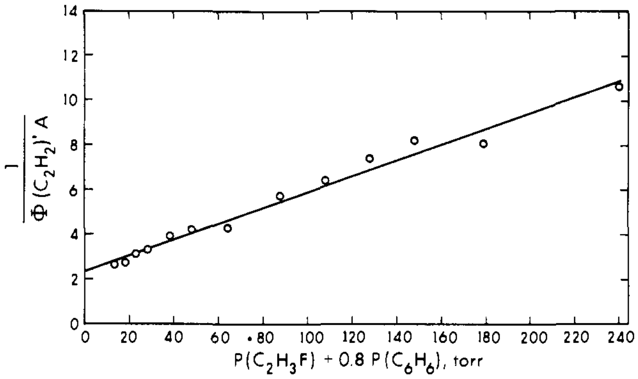


Figure 3. Plot of $\phi(C_2H_2)^{-1}$ corrected for quenching of ($^1B_{2u}$) benzene (vide infra) vs. total pressure in the benzene ($^3B_{1u}$) sensitized decomposition of C_2H_3F. Temperature: 27 °C.

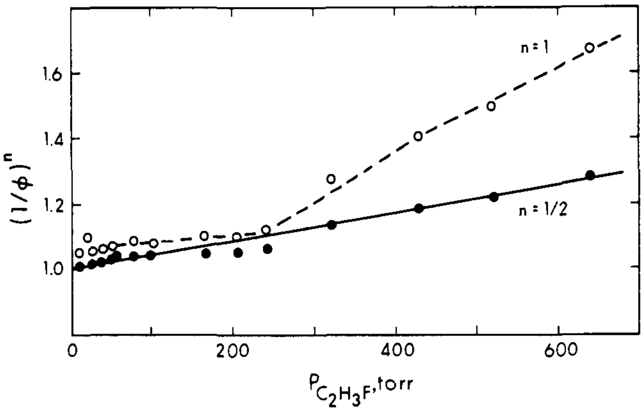


Figure 4. Plots of $\phi(C_2H_2)^{-1}$ and $\phi(C_2H_2)^{-1/2}$ vs. C_2H_3F pressure in the Hg ($^3P_1$) sensitized decomposition of C_2H_3F.

Table V. Rates of Acetylene and *trans*-2-Butene Formation from the Benzene ($^3B_{1u}$) Sensitization of Vinyl Fluoride in the Presence of *cis*-2-Butene[a]

$P(C_2H_3F)$, Torr	Time, min	Rates, µmol/(cm^3 min)		Φ	
		C_2H_2	*trans*-2-C_4H_8	C_2H_2	*trans*-2-C_4H_8
0	5	0	5.92×10^{-3}	0	1.000
4.16	5	1.66×10^{-4}	5.53×10^{-3}	0.0141	0.935
6.90	5	2.55×10^{-4}	4.86×10^{-3}	0.0216	0.821
10.0	5	3.06×10^{-4}	5.52×10^{-3}	0.0259	0.933
10.0	8	2.85×10^{-4}	5.02×10^{-3}	0.0241	0.849
15.0	5	3.44×10^{-4}	4.83×10^{-3}	0.0291	0.816
16.0	7	3.81×10^{-4}	4.94×10^{-3}	0.0322	0.835
18.9	5	4.09×10^{-4}	4.62×10^{-3}	0.0346	0.780
25.0	5	4.61×10^{-4}	4.34×10^{-3}	0.0390	0.733
29.7	5	4.97×10^{-4}	4.16×10^{-3}	0.0421	0.702

[a] (*cis*-2-C_4H_8) = $P(C_6H_6)$ = 10 Torr. T = 27 °C

$k_4(\mathrm{Hg}) = k_5(\mathrm{Hg}) = 3.8 \times 10^{10}\ \mathrm{s}^{-1}$, $k_2(\mathrm{Cd}) = 8.3 \times 10^8\ \mathrm{s}^{-1}$, and $k_2(\mathrm{C_6H_6}) = 4.6 \times 10^8\ \mathrm{s}^{-1}$. In line with current views on the triplet state decomposition of ethylenes we identify $C_2H_3F^*$ with the lowest triplet (π,π^*) state of vinyl fluoride and $C_2H_3F^{**}$ with the triplet ground state of 2-fluoroethylidene, $:CHCH_2F$. Furthermore, we consider the basic mechanism in all three systems to be identical, as has been shown to be the case for ethylene, and attribute the difference in the kinetic behavior of the various systems to the dependence of the rate constant values of the individual elementary reactions on excess energy.

Using simple RRK theory it can be shown that all three systems can be interpreted in terms of a two excited state mechanism having identical sets of Arrhenius parameters for the elementary reactions. Thus, in the RRK equation,[20]

$$k = A(1 - (E_a/E_t))^{s-1}$$

$s = 9.5$, $E_t = E_{\mathrm{total}} = E_{\mathrm{sensitizer}} - E_{\mathrm{excitation}} = 112.7 - 50$; $87.7 - 50$; and $84.4 - 50$ kcal/mol for Hg ($^3P_1$), Cd ($^3P_1$), and benzene ($^3B_{1u}$) sensitization, respectively, and we obtain for the rate coefficient of the decomposition step,

$$k_5 = (2.1 \pm 1.0) \times 10^{12} \exp((-22\,400 \pm 1\,700)/RT)\ \mathrm{s}^{-1}$$

For the isomerization reaction 4, the activation energy has been estimated[2] to be approximately 6.0 kcal/mol which, when combined with the rate constant of $3.8 \times 10^{10}\ \mathrm{s}^{-1}$ obtained for the mercury sensitized system, leads to a value of $9 \times 10^{10}\ \mathrm{s}^{-1}$ for the preexponential factor of reaction 4.

As seen from the data the isomerization rate constant is insensitive to the excitation energy of the sensitizer but the decomposition rate constant, owing to the higher activation energy involved, is highly sensitive and becomes the sole rate-controlling factor in the cadmium- and benzene-sensitized reactions.

The alternative isomerization reaction

$$C_2H_3F^* \rightarrow :CF\text{-}CH_3 \qquad (7)$$

giving 1-fluoroethylidene is slow with an estimated rate constant of $10^5\ \mathrm{s}^{-1}$ in the mercury-sensitized reaction[2] and consequently 1-fluoroethylidene is not considered to have a role in the decomposition sequence. The slowness of this reaction is related to the high energy of the lowest triplet state of 1-fluoroethylidene, which is about 99 kcal/mol above ground state vinyl fluoride.

The values derived for k_4 and k_5 above may be compared to the corresponding values for the triplet state reactions of ethylene, $1 \times 10^{11} \exp(-2500/RT)\ \mathrm{s}^{-1}$ and $1 \times 10^{13} \exp(-3500/RT)\ \mathrm{s}^{-1}$, respectively. If hydrogen loss from 2-fluoroethylidene would occur with the same rate coefficient as from ethylidene then, after making allowance for reaction path degeneracies, state energy, and effective number of oscillator differences, it can be estimated that in the mercury-sensitized reaction hydrogen loss should be slower than hydrogen fluoride loss by a factor of 2×10^{-2}. Since hydrogen formation could not be detected experimentally, the upper limit for the quantum yield of hydrogen formation is about 10^{-3}, suggesting that the activation energy for hydrogen elimination from 2-fluoroethylidene is somewhat higher than from ethylidene. This is in line with the computed enthalpy change difference of the overall reaction:

$$C_2H_4 \rightarrow C_2H_2 + H_2 \qquad \Delta H = 41\ \mathrm{kcal/mol}$$

$$C_2H_3F \rightarrow C_2HF + H_2 \qquad \Delta H \geqslant 43\ \mathrm{kcal/mol}$$

Returning to the question of the efficiencies of the quenching reactions 3 and 6, the suppressing effect of added *cis*-2-butene in the cadmium-sensitized reaction comes from two components, the competitive quenching of the excited sensitizer by C_2H_3F and *cis*-2-butene,

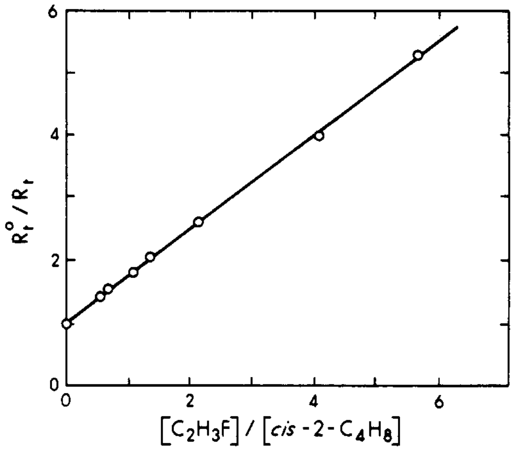


Figure 5. Plot of eq IV.

$$\mathrm{Cd}(^3P_1) + C_2H_3F \rightarrow \mathrm{Cd} + C_2H_3F^* \qquad (8)$$

$$\mathrm{Cd}(^3P_1) + cis\text{-}2\text{-}C_4H_8 \rightarrow \mathrm{Cd} + \tfrac{1}{2}(trans\text{-}2\text{-}C_4H_8) + \tfrac{1}{2}(cis\text{-}2\text{-}C_4H_8 \qquad (9)$$

and the quenching of excited C_2H_3F by *cis*-2-butene,

$$C_2H_3F^* + cis\text{-}2\text{-}C_4H_8 \rightarrow C_2H_3F + cis\text{-}2\text{-}C_4H_8 \qquad (10)$$

$$C_2H_3F^{**} + cis\text{-}2\text{-}C_4H_8 \rightarrow C_2H_3F + cis\text{-}2\text{-}C_4H_8 \qquad (11)$$

Steady-state treatment of steps 8 and 9 gives the kinetic relation

$$\frac{R_t^0}{R_t} = \frac{1}{2\phi_t} = 1 + \frac{k_8}{k_9}\frac{[C_2H_3F]}{[cis\text{-}C_4H_8]} \qquad (\mathrm{IV})$$

where R_t^0 and R_t represent the rates of *trans*-2-butene formation in the absence and presence of vinyl fluoride, respectively. From the slope of the linear plot shown in Figure 5 the ratio of k_8/k_9 has the value of 0.80 ± 0.04 at 275 °C indicating the previously noted electrophilic character of Cd ($^3P_1$) atoms.[21,22] It should also be mentioned here that, as has been previously shown, in the quenching reactions of Cd ($^3P_1$) atoms the $^3P_1$ and $^3P_0$ states are always present in near equilibrium distribution and therefore the quenching rate constants and excitation energies transferred represent an unspecified average between the $^3P_1$ and $^3P_0$ level values.

Now, it is possible to evaluate the efficiency of step 11 relative to steps 5 and 6. Neglecting the quenching of the short-lived $C_2H_3F^*$ intermediate, steady-state treatment of reactions 11, 5, and 6 yields, for the ratio of the quantum yields of acetylene formation in the absence and presence of *cis*-2-butene, the following equation,

$$\phi(C_2H_2)^0/\phi(C_2H_2)\left(1 + \frac{k_9[cis\text{-}2\text{-}C_4H_8]}{k_8[C_2H_3F]}\right) = 1 + \left(\frac{k_{11}}{k_5 + k_6[C_2H_3F]}\right)[cis\text{-}2\text{-}C_4H_8] \qquad (\mathrm{V})$$

The appropriate data are plotted in Figure 6. From the slope of the resultant straight line the value of k_{11}/k_6 is calculated to be 0.80. Thus, the deactivating efficiency of *cis*-2-butene is nearly equal to that of vinyl fluoride and probably both reactions proceed with gas kinetic collision frequency.

In the benzene-sensitization system the following sequence of elementary steps may be considered:

$$\mathrm{Be} + h\nu \rightarrow {}^1\mathrm{Be}^* \qquad (12)$$

$$^1\mathrm{Be}^* \rightarrow \mathrm{Be} + h\nu \qquad (13)$$

$$^1\mathrm{Be}^* \rightarrow {}^3\mathrm{Be}^* \qquad (14)$$

$$^1\mathrm{Be}^* + \mathrm{Be} \rightarrow 2\mathrm{Be} \qquad (15)$$

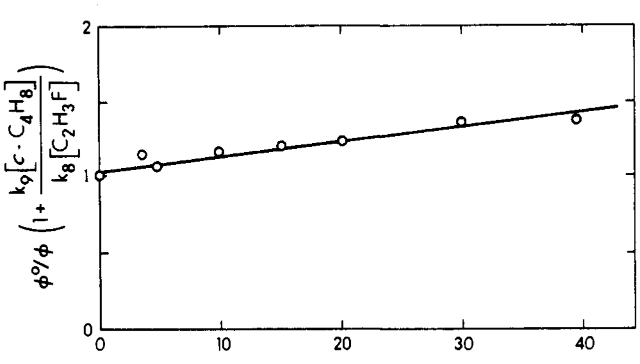


Figure 6. Plot of eq V.

$$^1Be^* + cis\text{-}2\text{-}C_4H_8 \rightarrow \text{reaction} \tag{16}$$

$$^1Be^* + C_2H_3F \rightarrow \text{reaction} \tag{17}$$

$$^3Be^* \rightarrow Be \tag{18}$$

$$^3Be^* + Be \rightarrow 2Be \tag{19}$$

$$^3Be^* + cis\text{-}2\text{-}C_4H_8 \rightarrow Be + \tfrac{1}{2}(cis\text{-}2\text{-}C_4H_8) + \tfrac{1}{2}(trans\text{-}2\text{-}C_4H_8) \tag{20}$$

$$^3Be^* + C_2H_3F \rightarrow Be + C_2H_3F^* \tag{21}$$

where Be is benzene. Under the experimental conditions which prevailed in the present study steps 15 and 16 are slow, $k_{16} \approx k_{15} \approx 6 \times 10^7$ l. mol^{-1} s^{-1},[23] relative to 13 and 14. $(k_{13} + k_{14}) = 1.7 \times 10^6$ s^{-1},[24] and can be neglected. Recently, Das Gupta and Phillips[25] reported a value for k_{17} of 1.75×10^8 l. mol^{-1} s^{-1} and consequently at higher C_2H_3F pressures quenching of singlet benzene by C_2H_3F will become significant, giving rise to the formation of the three isomeric adducts $C_2H_3F{\cdot}C_6H_6$ detected. A detailed discussion of adduct formation between *cis*-butene and benzene has been given by Morikawa, Brownstein, and Cvetanovic.[26] The lifetime of ($^3B_{1u}$) benzene at 20 Torr of benzene pressure has been determined to be 26 μs.[27] Recently Hunter and Stock have reported values for k_{18} and k_{19} of 1.7×10^3 s^{-1} and 6.6×10^7 l. mol^{-1} s^{-1}, respectively.[28] These lead to the effective lifetime of $\tau = (k_{18} + k_{19}[C_6H_6])^{-1} = 14$ μs for triplet state benzene at 20 Torr of benzene. The value[25] of the rate constant k_{20} is 9×10^9 l. mol^{-1} s^{-1} and thus, in the presence of 10 Torr of *cis*-butene, reactions 18 and 19 can be neglected and the expression for the rate of *trans*-2-butene formation simplified to $R_t^0 = \phi_t I_a/2$, where ϕ_t is the quantum yield of singlet → triplet intersystem crossing, 0.72 ± 0.02, and I_a is the absorbed light intensity.

Steady-state treatment of the simplified mechanism gives the following relation for the ratio of *trans*-2-butene formation in the absence and presence of C_2H_3F:

$$R_t^0/R_t = 1 + \frac{k_{21}}{k_{20}}\frac{[C_2H_3F]}{[cis\text{-}2\text{-}C_4H_8]} \tag{VI}$$

A plot of eq VI, Figure 7, gives a straight line from the slope of which the rate constant ratio k_{21}/k_{20} is estimated to have a value of 0.14 ± 0.01 in good agreement with Das Gupta and Phillips' results.[25] The corresponding value for ethylene[23,25,29,30] is 0.22, hence the ratio of the rate constants for quenching triplet benzene by C_2H_3F and C_2H_4 is 0.7, following the trend established earlier for the effect of fluorine substitution in the quenching of triplet mercury[31-33] and triplet cadmium atoms[19] manifesting the electrophilic nature of the energy donor.

To evaluate the relative efficiencies of C_2H_3F and benzene in quenching excited triplet C_2H_3F, the following scheme is considered:

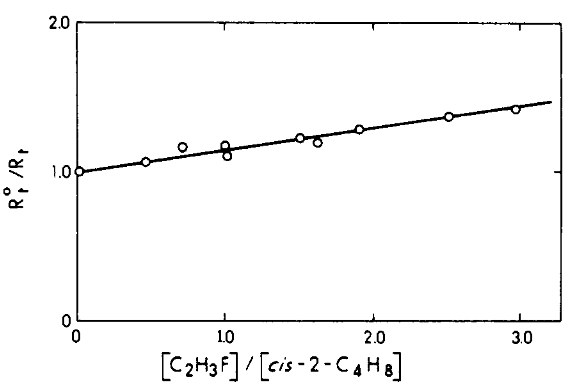


Figure 7. Plot of eq VI.

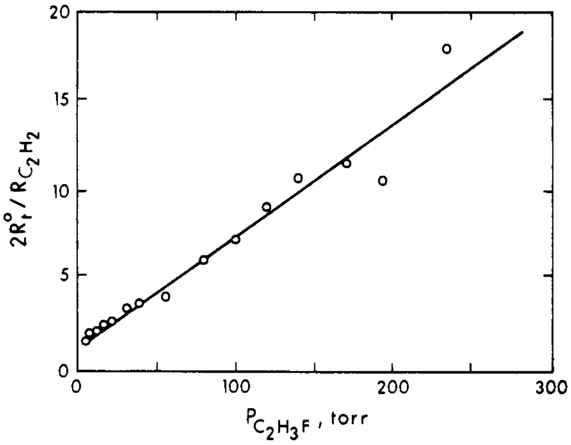


Figure 8. Plot of eq VII.

$$C_2H_3F^* \rightarrow C_2H_2 + HF \tag{2}$$

$$C_2H_3F^* + C_2H_3F \rightarrow 2C_2H_3F \tag{3}$$

$$C_2H_3F^* + Be \rightarrow C_2H_3F + Be \tag{22}$$

Steady-state treatment of this three-step scheme in the complete quenching region yields the kinetic relation,

$$\frac{2R_t^0}{R_{C_2H_2}} = 1 + \frac{k_{22}}{k_2}[Be] + \frac{k_3}{k_2}[C_2H_3F] \tag{VII}$$

The plot of eq VII, Figure 8, is a straight line with an intercept of 1.58 and slope of 0.071. From these k_{22}/k_2 is 0.8. Thus, benzene, *cis*-2-C_4H_8, and C_2H_3F are nearly equally efficient in deactivating triplet-excited C_2H_3F.

It is now possible to modify eq I for the benzene-sensitized decomposition of C_2H_3F. Since quenching of the $^1B_{2u}$ state of benzene by C_2H_3F is by no means negligible, the effect of singlet quenching on the acetylene yield must be taken into account. The modified form of eq I is:

$$\frac{1}{\phi(C_2H_2)'A} = B + \frac{k_3}{k_2}\{[C_2H_3F] + 0.8[Be]\}$$

where $\phi(C_2H_2)' = R(C_2H_2)/2R(trans\text{-}2\text{-}C_4H_8)$; $A = 1 + k_{17}[C_2H_3F]/(k_{13} + k_{14} + k_{15}[Be])$; and B is the zero pressure extrapolated value of $\phi(C_2H_2)'$. Substituting the numerical values for $k_{13} - k_{15}$ and k_{17} at 10 Torr benzene pressure we obtain the relation

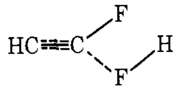
$$\frac{1.16}{R(C_2H_2)(1 + 100[C_2H_3F])} = B + \frac{k_3}{k_2}\{[C_2H_3F] + 0.8[Be]\} \tag{VIII}$$

The plot of the lhs vs. total pressure, Figure 3, gives a straight line from the slope of which the value of k_2 is calculated to be 4.6×10^8 s^{-1}, and the value of the zero pressure extrapolated quantum yield of acetylene formation, relative to *trans*-butene formation, is 0.43. The absolute value of the zero-pressure extrapolated quantum yield is 0.43 times the intersystem crossing efficiency of benzene, 0.72, that is, 0.31.

The large drop in the decomposition yield in going from the cadmium to the benzene system is interesting and can be attributed to the decrease in the triplet energy transferred to C_2H_3F, or possibly to some complications in the energy transfer mechanism[11,21,22,34] since the decrease in energy is only about 4.4 kcal/mol including the correction in heat capacity for the difference in temperature.[20] This phenomenon, namely the incompleteness of the reaction at zero pressure, is similar to that observed in the Cd ($^3P_1$) atom sensitized scrambling of 1,2-dideuterioethylene[10] and could perhaps also be attributed to intersystem crossing and to the long lifetime of the resultant, vibrationally excited ground state C_2H_3F.

If this is so then it would be required that the intersystem crossing efficiency be an inverse function of temperature since the measured rate constants in the cadmium and benzene system differ only by a factor of less than 2, whereas the percentage decomposition at zero pressure is different by a factor of more than 2. This may actually be the case because the intersection of the singlet ground state and lowest excited triplet surfaces occurs at low energies in ethylene and therefore it is conceivable that the transition probability decreases with increasing vibrational excitation.

Some years ago Clough, Polanyi, and Taguchi[35] observed infrared chemiluminescence from the HF product of the Hg ($^3P_1$) sensitized decomposition of CH_2CF_2. Emission was observed from the $\nu = 1\text{-}4$ levels, corresponding to up to 42.4 kcal/mol, together with considerable rotational excitation. This was accepted as a clear evidence against the formation of electronically excited C_2HF in the decomposition, in agreement with the conclusion of a concurrent, independent study.[2] Since the mechanisms of C_2H_3F and CH_2CF_2 decomposition are quite similar, the above argument can be extended to the decomposition of C_2H_3F. Also, the observed high-rotational excitation of HF could arise from the transfer of rotational momentum from the internal rotation of the difluoromethyl group in the triplet vinylidene, :CH—CHF_2, if it is assumed that the C-H bond cleavage is completed before the slowdown of the internal rotation takes place by the incipient triple bond



during the concerted intersystem crossing-decomposition step.

Acknowledgement. The authors thank the National Research Council of Canada for financial support and Drs. I. Safarik and E. M. Lown for helpful assistance.

References and Notes

(1) A. R. Trobridge and K. R. Jennings, *Trans. Faraday Soc.*, **61**, 2168 (1965).
(2) O. P. Strausz, R. J. Norstrom, D. Salahub, R. K. Gosavi, H. E. Gunning, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **92**, 6395 (1970).
(3) M. G. Bellas, J. K. S. Wan, W. F. Allen, H. E. Gunning, and O. P. Strausz, *J. Phys. Chem.*, **68**, 2170 (1964).
(4) R. J. Cvetanovic, *Prog. React. Kinet.*, **2**, 39 (1964).
(5) A. B. Callear and R. J. Cvetanovic, *J. Chem. Phys.*, **24**, 873 (1956).
(6) D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Am. Chem. Soc.*, **85**, 862 (1963).
(7) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
(8) T. Terao, S. Hirokami, S. Sato, and R. J. Cvetanovic, *Can. J. Chem.*, **44**, 2173 (1966).
(9) S. Hirokami and S. Sato, *Can. J. Chem.*, **45**, 3181 (1967).
(10) S. Tsunashima, S. Hirokami, and S. Sato, *Can. J. Chem.*, **46**, 995 (1968).
(11) H. E. Hunziker, *J. Chem. Phys.*, **50**, 1288 (1969).
(12) R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959).
(13) S. Tsunashima and S. Sato, *Bull. Chem. Soc. Jpn.*, **41**, 284 (1968).
(14) H. E. Hunziker, *J. Chem. Phys.*, **50**, 1294 (1969).
(15) R. B. Cundall and D. G. Milne, *J. Am. Chem. Soc.*, **83**, 3902 (1961).
(16) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).
(17) S. Sato, K. Kikuchi, and M. Tanaka, *J. Chem. Phys.*, **39**, 237 (1963).
(18) M. Tanaka, T. Terao, and S. Sato, *Bull. Chem. Soc. Jpn.*, **38**, 1645 (1965).
(19) M. Tanaka, K. Kato, and S. Sato, *Bull. Chem. Soc. Jpn.*, **39**, 1423 (1966).
(20) Using the vibrational frequencies reported by P. Torkengton and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945), the difference in heat capacity of the vibrations of C_2H_3F between 27 and 275 °C was estimated to be 1.9 kcal/mol. The RRK expression for the cadmium system was corrected accordingly.
(21) P. Young, E. Hardwidge, S. Tsunashima, G. Greig, and O. P. Strausz, *J. Am. Chem. Soc.*, **96**, 1946 (1974).
(22) P. Young, G. Greig, and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 413 (1970).
(23) A. Morikawa and R. J. Cvetanovic, *J. Chem. Phys.*, **49**, 1214 (1968).
(24) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961).
(25) G. Das Gupta and D. Phillips, *J. Phys. Chem.*, **76**, 3668 (1972).
(26) A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **92**, 1471 (1970).
(27) C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1998 (1967).
(28) T. F. Hunter and M. G. Stock, *Chem. Phys. Lett.*, **22**, 368 (1973).
(29) E. K. C. Lee, H. O. Denschky, and G. A. Hanninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968).
(30) G. A. Hanninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).
(31) A. R. Trobridge and K. R. Jennings, *Proc. Chem. Soc.*, 335 (1964).
(32) A. J. Yarwood, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **41**, 1705 (1964).
(33) M. G. Bellas, Y. Rousseau, O. P. Strausz, and H. E. Gunning, *J. Chem. Phys.*, **41**, 768 (1964).
(34) W. H. Breckenridge, T. W. Broadbent, and D. S. Moore, *J. Phys. Chem.*, **79**, 1233 (1975).
(35) P. N. Clough, J. C. Polanyi, and R. T. Taguchi, *Can. J. Chem.*, **48**, 2919 (1970).