

THE Hg 6(³P₁) PHOTSENSITIZED DECOMPOSITION OF 1,1,2,2-TETRAFLUOROCYCLOBUTANE

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Summary

The Hg 6(³P₁) photosensitized decomposition of 1,1,2,2-tetrafluorocyclobutane (c-C₄H₄F₄) was carried out by irradiating a mixture (50 or 150 Torr) of c-C₄H₄F₄ and mercury vapor with 253.7 nm radiation from a low pressure mercury lamp. The photolysis of a mixture of hydrogen and a small amount of c-C₄H₄F₄ was also carried out to investigate the reactions of hydrogen atoms with c-C₄H₄F₄. Using the chemical method of Cvetanovic, the quenching cross section of c-C₄H₄F₄ was determined to be 0.3 Å² relative to that of N₂O.

Major products in the photolysis of the Hg/c-C₄H₄F₄ system and their relative initial yields include HF (1.0), H₂ (0.06), CH₄ (0.04), C₂H₆ (0.10), C₂F₄ (0.02), C₂H₂F₂ (0.01), C₂HF₃ (0.13), c-C₃H₂F₄ (0.34), two isomers of C₆H₄F₆ (0.84 total), C₈H₆F₈ (0.22) and an uncharacterized C₈ product (about 0.1). One of the C₆H₄F₆ isomers and all the lower molecular weight products except C₂F₄ were also formed in the system containing excess H₂.

It is suggested that the major primary process in the chemical quenching of Hg 6(³P₁) by c-C₄H₄F₄ is rupture of the C—H bond to form H· and c-C₄H₃F₄·. The low quantum yield of the primary process and the low efficiency of hydrogen abstraction from the substrate to form H₂ are consistent with an earlier generalization that both processes occur efficiently in fluorohydrocarbons only if H and F occur on the same carbon centers. Alternative, more favorable routes of attack by the H atom on the substrate appear to be fluorine abstraction and ring opening.

Introduction

The present investigation of the mercury sensitized photolysis of 1,1,2,2-tetrafluorocyclobutane was undertaken in parallel with studies of the gamma radiolysis [1], mass spectrometric fragmentation [2], and ion-molecule reactions of this compound [3]. It was expected that mechanistic information derived from the photolytic (and mass spectrometric) studies would aid in interpretation of the more complex radiolytic system [4].

Mercury $6(^3P_1)$ photosensitized decomposition studies on a large number of alkanes and cycloalkanes have established that C—H bond rupture is the primary quenching process in these systems [5, 6]. Only a limited amount of work has appeared dealing with mercury sensitized decomposition of perfluorocarbons (whether open chain or cyclic); details of the decomposition mechanism have not been established [7]. There have been no previously reported investigations of the mercury sensitized decomposition of partially fluorinated cyclobutanes or other cycloalkanes. However, experiments reported by Scott and Jennings on the mercury sensitized photolysis of C_2H_5F , CH_3CHF_2 and CH_3CF_3 provides some guidelines for the behavior of partially fluorinated hydrocarbons under these conditions [8].

The main conclusions which can be drawn from the work of Scott and Jennings are as follows: (1) in these systems, as in the simple alkanes and cycloalkanes, chemical quenching of excited mercury atoms involves scission of C—H bonds; (2) fluorohydrocarbons react efficiently in mercury sensitized photolysis only if the molecule contains both fluorine atoms and hydrogen atoms on the same carbon; (3) the hydrogen atoms produced in the primary quenching process tend to abstract hydrogen from the substrate to form H_2 , but again the process occurs efficiently only at a carbon atom which carries both fluorine and hydrogen substituents; (4) recombination of $H\cdot$ atoms and fluoroalkyl radicals produces chemically activated molecules which tend to eliminate HF. It will be seen that these principles aid in interpreting the behavior of *c*- $C_4H_4F_4$ in mercury sensitized photolysis, but that the considerable ring strain in the molecule and the lack of carbon sites carrying both hydrogen and fluorine lead to some deviations from the patterns of reactivity seen by Scott and Jennings.

Experimental section

Sample preparation

The vessel used in the photolysis experiments had a volume of 91 cm^3 ; it was constructed of 18 mm ID GE type 204 clear fused quartz and was equipped with a glass break seal and a side arm (Fig. 1). To clean the vessel between experiments, it was soaked in nitric acid overnight to remove inorganic material (especially mercury), rinsed with distilled water and annealed at 565°C to pyrolyze any organic materials on the walls. Before introducing the sample a drop of triple-distilled mercury was placed in the vessel, and the vessel was pumped on for at least 6 h. In the case of photolysis of the pure system samples of *c*- $C_4H_4F_4$ were measured in a standard volume using the *PVT* technique, were transferred to the photolysis vessel and were sealed under vacuum. For photolysis of a mixture of hydrogen and *c*- $C_4H_4F_4$, the tetrafluorocyclobutane was introduced as above, the photolysis vessel was immersed in liquid nitrogen and hydrogen was metered directly into the photolysis vessel. After the introduction of hydrogen, the vessel was very cautiously sealed. The pressure of hydrogen in the vessel at room temperature

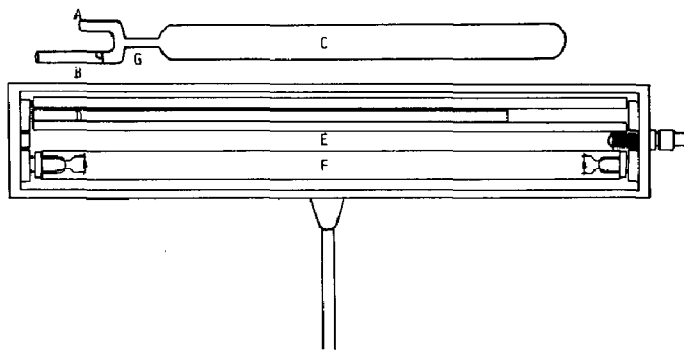


Fig. 1. The photolysis set-up: A, mercury drop; B, break seal; C, reaction cell; D, glass tube to support the photolysis vessel; E, desk lamp fixture; F, germicidal lamp; G, graded seal.

(297 K) would be 3.87 (*i.e.* 297 K/77 K) times the measured pressure. For quenching cross section and actinometry experiments, $c\text{-C}_4\text{H}_4\text{F}_4$ was introduced as in the case of the pure system; a pre-measured amount of N_2O from a standard vessel was vacuum transferred into the photolysis vessel and was sealed under vacuum. The purification of $c\text{-C}_4\text{H}_4\text{F}_4$ is described elsewhere [1, 4]. Nitrous oxide obtained from the Matheson Gas Company was subjected to at least 10 freeze-pump-thaw cycles to remove air before use; C.P. grade Matheson H_2 was used as received.

Sample irradiation

To maintain a constant mercury vapor pressure in mercury sensitization experiments, it is common to provide a small drop of liquid mercury in direct contact with the vapor phase. To obtain reproducible results, however, we found it necessary to make sure that the drop was in a small side arm and not in the main reaction cell exposed to the full lamp intensity.

The source of 253.7 nm light was a General Electric 15 W Germicidal lamp (type G15T8), which is essentially a low pressure mercury lamp in a high silica envelope which transmits 253.7 nm and not 184.9 nm (Fig. 1). This lamp was mounted inside a standard desk lamp fixture equipped to hold two fluorescent tubes. The second lamp was replaced by a stack of Pyrex tubes which provided reproducible positioning of the sample vessel. To avoid intensity variations due to a.c. line voltage fluctuations, a Sola saturable core transformer was used to power the lamp. The photolysis arrangement was covered with a wooden eye shield and air was blown through this set-up to remove any ozone formed and to keep the temperature constant. The temperature was recorded using a thermometer with its bulb resting inside the photolysis cavity. This experimental arrangement is essentially the same as the one described in detail by Frank [9]. After photolysis the sample was cooled down to liquid nitrogen temperature to prevent any dark reactions.

Product identification and analysis

The organic product identification was done using an on-line combination of a gas chromatograph (GC) and a mass spectrometer. Hydrogen was

measured by the conventional arrangement of a Toepler pump and a McLeod gauge and the organic products were measured by flame ionization gas chromatography. The potentiometric titration technique used to measure HF [4, 10], as well as other details of product identification and analysis [1, 4], are described elsewhere.

Nitrogen formed in the photolysis of a mixture of N_2O and $c-C_4H_4F_4$ was transferred from the photolysis vessel immersed in liquid nitrogen via a Toepler pump into a McLeod gauge where it was measured.

Results

Quenching cross section measurements and actinometry

For quenching cross section measurements and actinometry, four mixtures with different pressure ratios of $c-C_4H_4F_4$ to N_2O ($P_{c-C_4H_4F_4}/P_{N_2O}$) were photolysed for 30 s. In each sample the total pressure was 50 Torr. A plot of the reciprocal of the number of moles of nitrogen formed in each mixture against the quantity $P_{c-C_4H_4F_4}/P_{N_2O}$ gave a straight line, as shown in Fig. 2. The intercept of this line gives the reciprocal of the number of moles of nitrogen formed in pure N_2O . The amount of nitrogen formed in the absence of $c-C_4H_4F_4$ was found to be $9.597 \mu\text{mol}$. Assuming a quantum yield of 0.8 for N_2 production in mercury sensitized photolysis of N_2O [6] the absorbed light intensity was calculated to be 2.4×10^{17} quanta s^{-1} in the 91 cm^3 vessel (*i.e.* $24 \mu\text{einstein min}^{-1}$)*. The quenching cross section of $c-C_4H_4F_4$ was determined relative to that of nitrous oxide [6]. The ratio β of the relative quenching rates for $c-C_4H_4F_4$ and nitrous oxide was calculated from the slope of the line in Fig. 2 to be

$$\beta = (\text{slope}) \times (\text{number of photons absorbed in 30 s}) / \text{Avogadro's number}$$

$$\beta = 0.0102$$

The quenching cross section of $c-C_4H_4F_4$ was calculated using the equation [6]

$$\frac{\sigma_{c-C_4H_4F_4}^2}{\sigma_{N_2O}^2} = \beta \left(\frac{1 + M_{Hg}/M_{N_2O}}{1 + M_{Hg}/M_{c-C_4H_4F_4}} \right)^{1/2}$$

where σ^2 is the quenching cross section and M the molecular weight of the species shown by the subscripts. Assuming the quenching cross section of N_2O determined by the chemical method to be 18 \AA^2 [6], $\sigma_{c-C_4H_4F_4}^2$ is calculated to be 0.27 \AA^2 . Recently Gleditsch and Michael [11] have given a value of 22.1 \AA^2 as the preferred value for $\sigma_{N_2O}^2$. Using this value of $\sigma_{N_2O}^2$, the corresponding value of $\sigma_{c-C_4H_4F_4}^2$ is 0.31 \AA^2 .

*The absorbed intensity reported here is about four times higher than an extrapolated value of the incident light intensity measured for the same lamp by Frank [9]. The high intensity absorbed by Hg atoms may be due to "trapping" of the 253.7 nm Hg radiation which is not the resonance radiation but behaves as if it were.

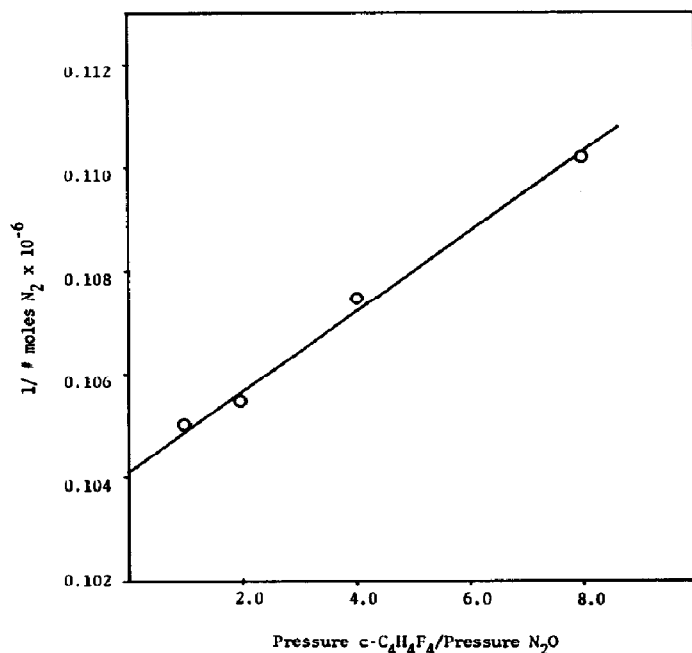
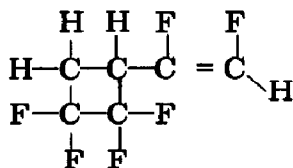


Fig. 2. Modified Stern-Volmer plot; a plot of the reciprocal of the number of moles of N_2 against the ratio of the pressure of $c\text{-C}_4\text{H}_4\text{F}_4$ to that of N_2O .

Photolysis products

The major products formed in the photolysis of $c\text{-C}_4\text{H}_4\text{F}_4$ at 50 Torr are HF, C_2H_6 , $C_3F_4H_2$, two isomers of $C_6H_4F_6$ (hereafter referred to as $C_6H_4F_6$ (I) and $C_6H_4F_6$ (II)), an unidentified C_8 compound and $C_8H_6F_8$ (a bicyclic compound); the minor products were H_2 , CH_4 , C_2F_4 , 1,1-difluoroethylene (1,1- $C_2H_2F_2$) and C_2F_3H . There were at least two more products whose yields were not recorded since they were formed in very small quantities and their compositions were unknown. Based upon the ^{19}F NMR and the mass spectral cracking pattern the probable structure of $C_6H_4F_6$ (I) is as follows:



The other isomer, $C_6H_4F_6$ (II), is probably non-cyclic as indicated by its proton NMR. We could determine neither the structure nor the exact composition of the C_8 compound. Further discussions of the composition and structure of some of the photolysis products are given elsewhere [1, 4].

A series of experiments was performed to investigate the dependence of product yields on photolysis time in pure 1,1,2,2-tetrafluorocyclobutane. These experiments were carried out at both 50 and 150 Torr of the tetrafluorocyclobutane to reveal a possible pressure effect. The yields of C_2H_6 and two isomers of $C_6H_4F_6$ increased linearly with irradiation time. The rest of

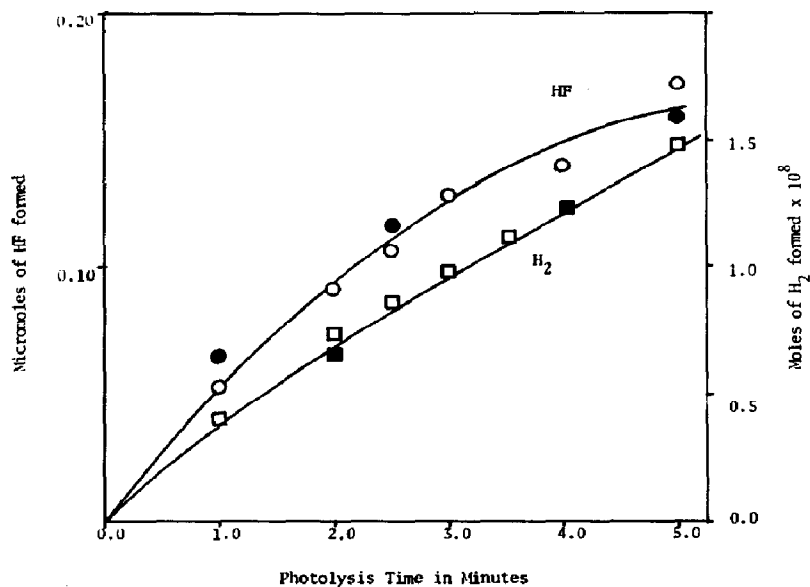


Fig. 3. Yield of HF (○ at 50 Torr, ● at 150 Torr) and H₂ (□ at 50 Torr, ■ at 150 Torr) as a function of time in the photolysis of *c*-C₄H₄F₄.

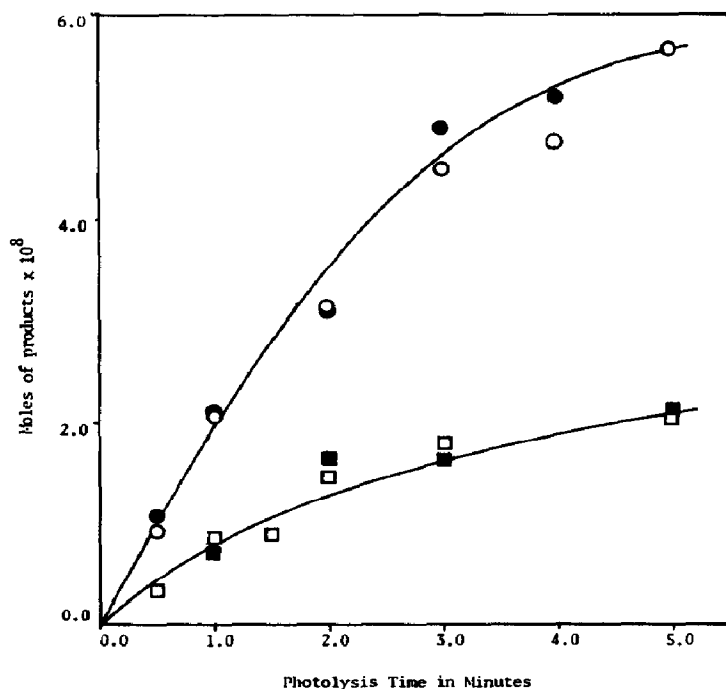


Fig. 4. Yield of C₃H₂F₄ (○ at 50 Torr, ● at 150 Torr) and C₂HF₃ (□ at 50 Torr, ■ at 150 Torr) as a function of time in the photolysis of *c*-C₄H₄F₄.

the products were formed at a decreasing rate at longer irradiation times and many of the yields approached limiting values after 2 min of photolysis. Figures 3 - 7 show the yield *versus* photolysis time plots for all products at

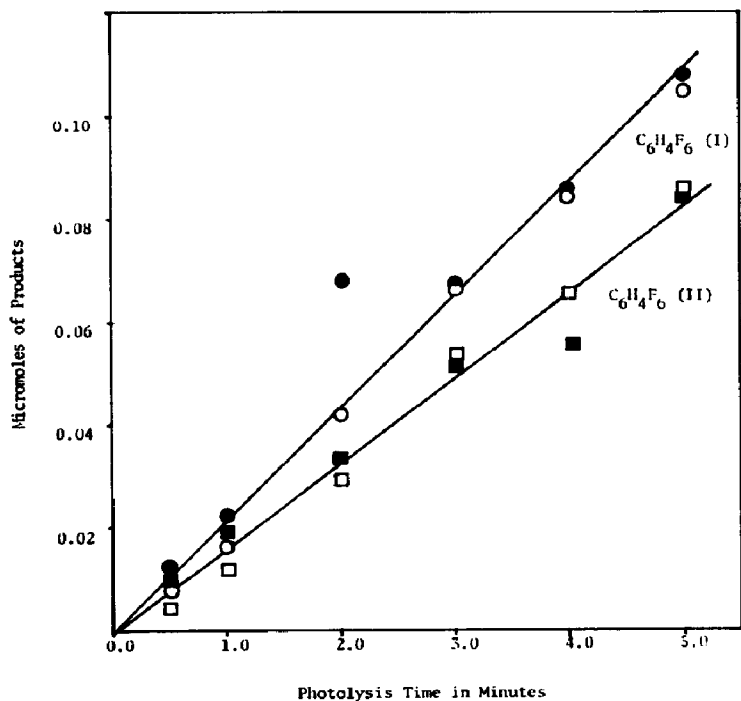


Fig. 5. Yield of $C_6H_4F_6$ (I) (\circ at 50 Torr, \bullet at 150 Torr) and $C_6H_4F_6$ (II) (\square at 50 Torr, \blacksquare at 150 Torr) as a function of time in the photolysis of $c-C_4H_4F_4$.

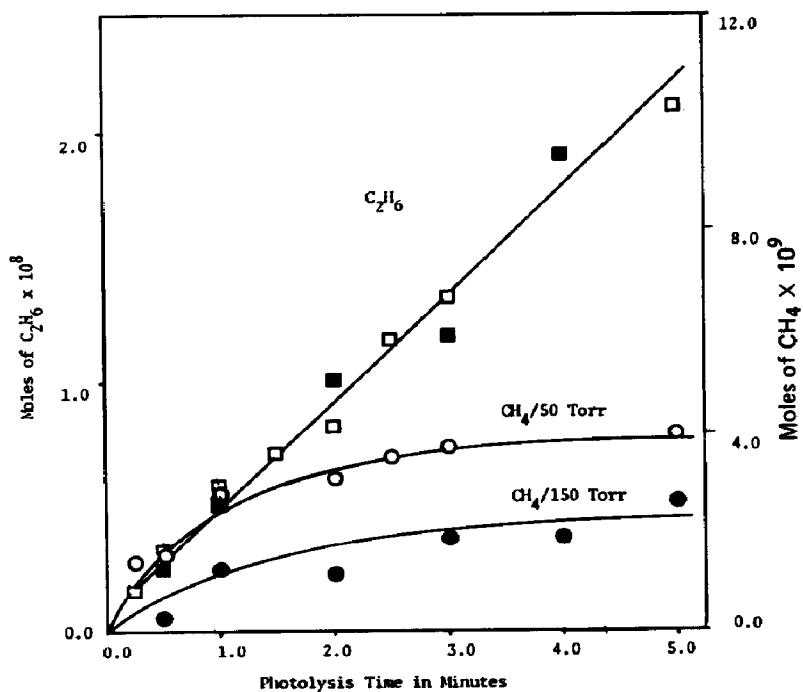


Fig. 6. Yield of C_2H_6 (\square at 50 Torr, \blacksquare at 150 Torr) and CH_4 (\circ at 50 Torr, \bullet at 150 Torr) as a function of time in the photolysis of $c-C_4H_4F_4$.

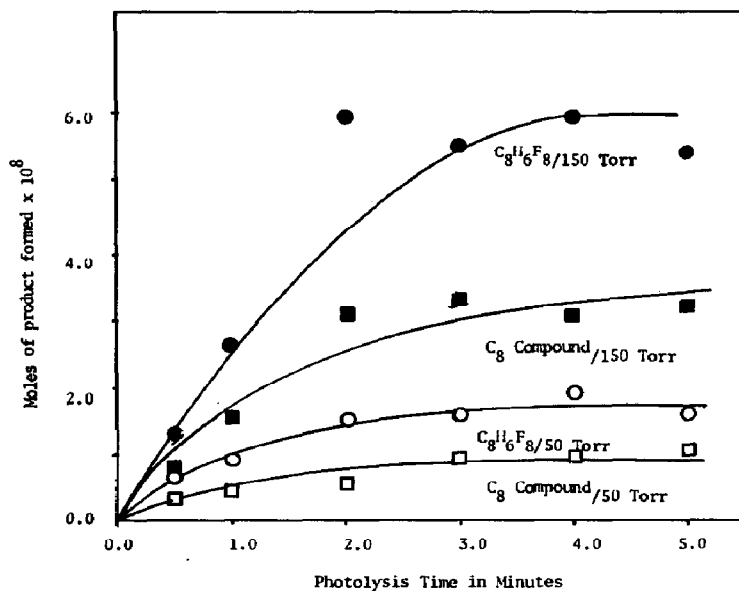


Fig. 7. Yield of $C_8H_6F_8$ (\circ at 50 Torr, \bullet at 150 Torr) and the C_8 compound (\square at 50 Torr, \blacksquare at 150 Torr) as a function of photolysis time.

TABLE 1

Relative yields of products formed in photolysis of $c-C_4H_4F_4$ systems

Product	Pure system ^a	H ₂ mixtures ^b
HF	1.0	1.0
H ₂	0.063	c
CH ₄	0.04	0.0082
C ₂ H ₆	0.10	0.053
C ₂ F ₄	0.016	- ^d
C ₂ H ₂ F ₂	0.010	0.0090
C ₂ HF ₃	0.13	0.13
<i>c</i> -C ₃ H ₂ F ₄	0.34	0.0106
C ₆ H ₄ F ₆ (I)	0.50	0.0082
C ₆ H ₄ F ₆ (II)	0.34	-
C ₈ ?	0.10	-
C ₈ H ₆ F ₈	0.22	-

^aFor 120 s photolysis of 50 Torr of $c-C_4H_4F_4$; actual yield of HF was 0.091 μ mol and $\phi(\text{HF}) = 0.0019$.

^bFor 300 s photolysis of 400 Torr of H₂ and 20 Torr of $c-C_4H_4F_4$; actual yield of HF was 0.235 μ mol.

^cNot measurable owing to presence of excess H₂.

^dDash indicates not observed.

both pressures. Relative yields for all products at 120 s photolysis time for a 50 Torr sample are shown in Table 1, normalized to an HF yield of 1.00 in order to give a clearer picture of the behavior of the system. The table also lists relative yields in the H_2 - $c\text{-C}_4\text{H}_4\text{F}_4$ system described below.

Since the yields of CH_4 , the C_8 compound and $\text{C}_8\text{H}_6\text{F}_8$ at 150 Torr were different from those at 50 Torr, a series of 120 s irradiations were carried out using pure $c\text{-C}_4\text{H}_4\text{F}_4$ at three more pressures ranging from 10 to 150 Torr. Yields of all the products except CH_4 , the C_8 uncharacterized compound and $\text{C}_8\text{H}_6\text{F}_8$ were independent of pressure above 30 Torr within experimental error. The yields of methane decreased with increase in pressure while those of the C_8 compound and $\text{C}_8\text{H}_6\text{F}_8$ increased linearly as shown in Fig. 8.

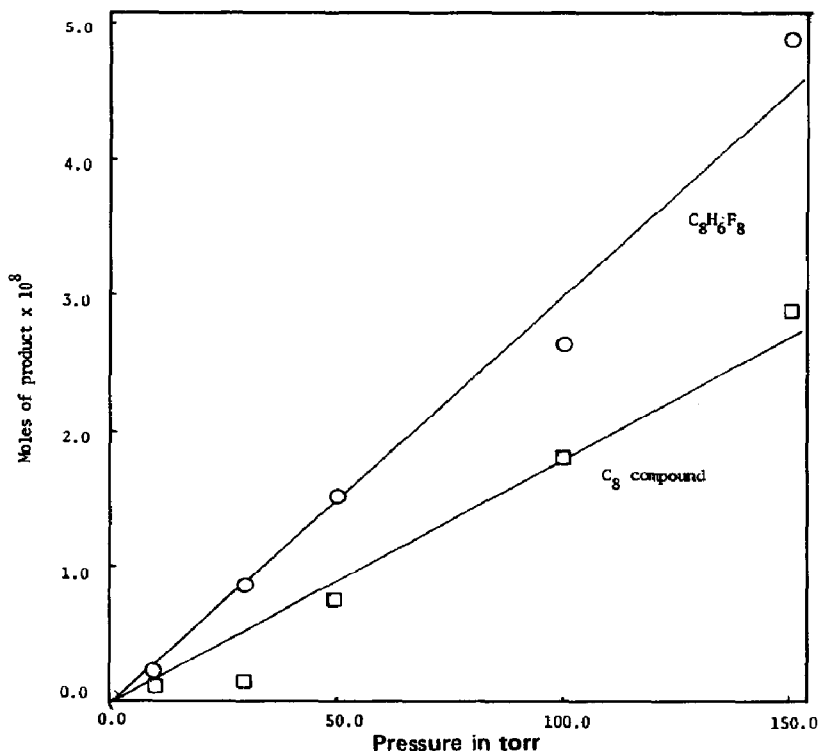


Fig. 8. Plots of yields of $\text{C}_8\text{H}_6\text{F}_8$ (\circ) and the C_8 compound (\square) as a function of pressure in the photolysis vessel.

To establish whether any of the products were due to the reactions of hydrogen atoms, a mixture of 400 Torr of H_2 and 20 Torr of $c\text{-C}_4\text{H}_4\text{F}_4$ was photolysed for 300 s. All the products formed in the pure system were formed except C_2F_4 , $\text{C}_6\text{H}_4\text{F}_6$ (II), the C_8 compound and $\text{C}_8\text{H}_6\text{F}_8$. The relative yields of products formed in this experiment are given in Table 1.

The material balance in the photolysis is reasonably good. The ratio of C/H/F is 4.00/3.65/4.48 when the photolysis has progressed for 120 s. This

shows a shortage of carbon and hydrogen. However, at shorter photolysis times the material balance is better, and at longer photolysis times worse. This indicates the formation of polymers or products which were not analyzable by the methods used in these experiments.

Discussion

The possibility of direct photolysis of $c\text{-C}_4\text{H}_4\text{F}_4$ by 253.7 nm light can be ignored since $c\text{-C}_4\text{H}_4\text{F}_4$ has no absorption above 180.0 nm*. Hence, all of the observed products in these experiments must be due to the quenching of Hg $6(^3\text{P}_1)$ to the $6(^1\text{S}_0)$ ground state by $c\text{-C}_4\text{H}_4\text{F}_4$. (Although it is possible to quench Hg $6(^3\text{P}_1)$ to the $6(^3\text{P}_0)$ state, this process has been shown to be unimportant in many systems [12] and we ignore it for lack of any direct evidence.) That $c\text{-C}_4\text{H}_4\text{F}_4$ is not very efficient in quenching the Hg $6(^3\text{P}_1)$ is shown by its relatively small value of 0.3 \AA^2 for the quenching cross section (based on a value of 18 \AA^2 for $\sigma_{\text{N}_2\text{O}}^2$). This inefficiency in quenching is in accordance with the generalization, discussed by Cvetanovic [6], that cycloalkanes are analogous to alkanes in their low quenching efficiency. A value of 0.3 \AA^2 for $\sigma_{c\text{-C}_4\text{H}_4\text{F}_4}^2$ is similar to the reported quenching cross sections of three partially fluorinated alkanes, $\text{CH}_3\text{CH}_2\text{F}$ (0.46 \AA^2), CH_3CHF_2 (0.45 \AA^2) and CH_3CF_3 (0.45 \AA^2) [8]. As expected this value for the quenching cross section of $c\text{-C}_4\text{H}_4\text{F}_4$ is considerably smaller than those of comparable alkanes or cycloalkanes but larger than those of perfluoroalkanes (e.g. $\sigma_{c\text{-C}_4\text{H}_4}^2 = 6.7 \text{ \AA}^2$ and $\sigma_{\text{CF}_4}^2 \ll 0.005 \text{ \AA}^2$) [6, 12].

The primary photophysical event and the subsequent quenching are shown in the following reactions:



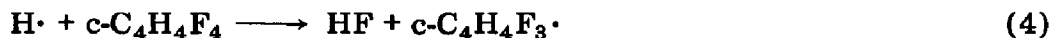
It is suggested that the quenching of Hg $6(^3\text{P}_1)$ by $c\text{-C}_4\text{H}_4\text{F}_4$ leads to the scission of a C—H bond (reaction (2)) because of the following three reasons: (a) C—H bond rupture has been established to be a major quenching process in cycloalkanes [6, 13]; (b) the products formed in photolysis of pure $c\text{-C}_4\text{H}_4\text{F}_4$ and those in a mixture of a large amount of hydrogen and a small amount of $c\text{-C}_4\text{H}_4\text{F}_4$ are similar, suggesting that hydrogen atoms are formed in the quenching process in this system; (c) when a mixture of $c\text{-C}_4\text{H}_4\text{F}_4$ and I_2 was photolyzed in the presence of mercury vapor, all the products in the photolysis were eliminated and a new product identified as $c\text{-C}_4\text{H}_3\text{F}_4\text{I}$ was formed. (Identification was based on the GC retention time and the mass spectral fragmentation pattern.)

*We recorded the ultraviolet absorption spectrum of $c\text{-C}_4\text{H}_4\text{F}_4$ using a McPherson Model 218 vacuum ultraviolet monochromator with double beam attachment and ratio-recording electronics and found that this compound does not absorb above 180.0 nm.

The work of Scott and Jennings indicates that H atoms abstract hydrogen from the substrate to form H₂ with good efficiency only if the parent molecule contains both H and F bonded to the same carbon atom. Since this is not the case with 1,1,2,2-tetrafluorocyclobutane, the hydrogen abstraction reaction would be expected to occur with low efficiency:

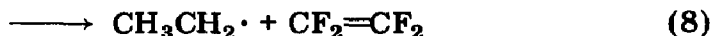
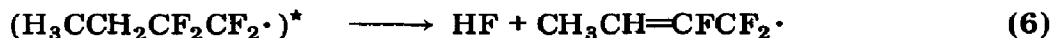


This expectation is confirmed by the low yield of H₂ relative to HF and other products. We suggest that the geometry and bonding situation in c-C₄H₄F₄ enhances the occurrences of two other reaction channels for hydrogen atoms, namely F atom abstraction and ring opening:



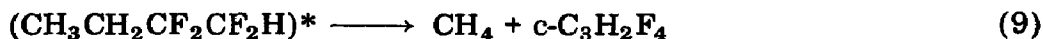
The near 90° bond angles in tetrafluorocyclobutane prevent good sp³ hybridization, decreasing sigma bond energies and enhancing accessibility of both the carbon atom and the substituents to attack. As discussed below, formation of C₂HF₃ provides support for the occurrence of reaction (4); some of the HF would also be formed this way. It is suggested that CH₄, c-C₃H₂F₄ and probably some of the C₂H₆ result from reaction (5).

The fates of the three radicals c-C₄H₃F₄·, (CH₃CH₂CF₂CF₂·)* and c-C₄H₄F₃· (formed in reactions (3) - (5)) determine the products formed and their relative distribution observed in the mercury sensitized photolysis of c-C₄H₄F₄. Since reaction (5) involves formation of a primary C—H bond (about 98 kcal mol⁻¹ [14]) and rupture of a weak C—C bond (61 kcal according to our measurements [2]) plus relief of ring strain, which we estimate as about 38 kcal, the product radical will be excited by as much as 75 kcal, probably mostly in the form of vibrational energy. This amount of energy is easily sufficient to cause fragmentation of the excited butyl radical via several competing pathways:



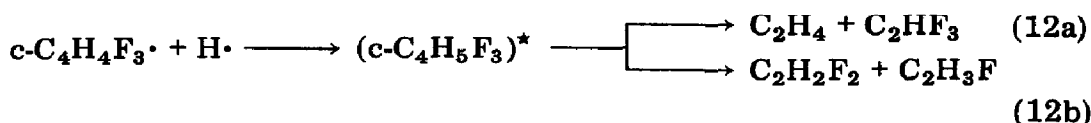
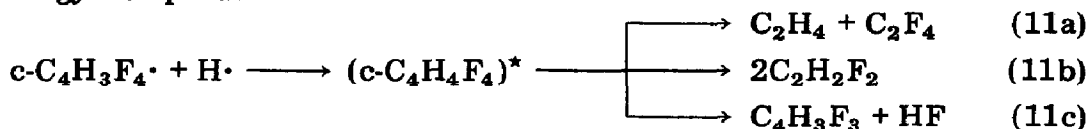
Of these three processes reaction (6) would be most favorable energetically being only about 15 kcal endoergic. However, owing to the high internal energy in the reactant, the relative pre-exponential factors would be expected to control the branching ratio; in fact, no product corresponding to the butenyl radical was seen. Since CH₃· and C₂H₅· could react with H· atoms or could abstract hydrogen from the substrate, the two reactions would account for formation of CH₄, c-C₃H₂F₄, C₂H₆ and C₂F₄, all of which are observed. In fact, there are no other obvious routes to methane or tetrafluorocyclopropane. Ethane could be formed by hydrogenation of ethylene, but this seems unlikely since an induction period for ethane formation would then be expected whereas the observed production graph is linear (Fig. 6). Conceivably, formation of methane and tetrafluorocyclopropane could

result from the thermalization of the excited tetrafluorobutyl radical followed by reaction with hydrogen atoms and fragmentation of the resultant excited butane:



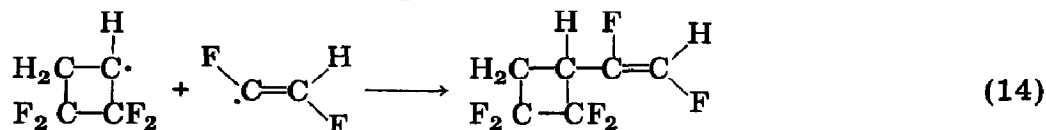
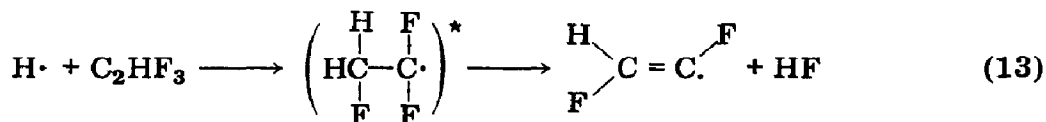
Reactions analogous to (9) and (10) have been seen in the pyrolysis of n-butane (although propylene rather than cyclopropane was reported) [13]. However, the direct fragmentation of reactions (7) and (8) seems more probable since the excited precursor is unlikely to persist long enough to become thermalized.

The cyclobutyl radicals formed in reactions (2) and (4) could combine to give C_8 species; a product $\text{C}_8\text{H}_6\text{F}_8$ corresponding to a dimer of $\text{c-C}_4\text{H}_3\text{F}_4\cdot$ was seen as well as another uncharacterized C_8 product. The radicals could also combine with hydrogen atoms, generally followed by fragmentation of the energy rich product:



(Thermalization is possible but is not shown.) Several of the predicted products were seen including C_2F_4 , $\text{C}_2\text{H}_2\text{F}_2$, and C_2HF_3 . Two others, namely $\text{C}_4\text{H}_3\text{F}_3$ and $\text{C}_2\text{H}_3\text{F}$, were not seen in mercury sensitized photolysis but were found in the gamma radiolysis of 1,1,2,2-tetrafluorocyclobutane and may be formed by the route indicated.

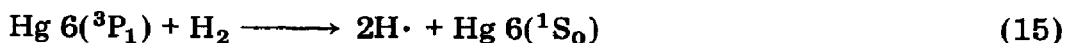
A possible problem in interpretation of the present results is the route to formation of the major C_6 products, particularly $\text{C}_6\text{H}_4\text{F}_6$ (I). Formation of C_2HF_3 in reaction (12a) does suggest one route to this product:



Alternatively, HF elimination could occur subsequent to reaction (14) or the cyclobutyl radical could first react with olefin, followed by subsequent reaction with a hydrogen atom and elimination of HF. Energy release in reaction (14) could easily lead to ring opening, accounting for $\text{C}_6\text{H}_4\text{F}_6$ (II). The reaction scheme suggested may be unable to account for the large yields of the two

C_6 species, however. A desirable reaction path would seem to be a combination of two cyclobutyl radicals with the opening of one (or both) of the rings, followed by elimination of a C_2 fragment (and possibly HF as well). All such sequences which we have devised require migration of a hydrogen or fluorine atom, however.

It was possible to study the somewhat simpler reactions resulting from combination of $H\cdot$ atoms and fluorobutyl radicals in the absence of the mutual reactions of fluorobutyl radicals by photolyzing mixtures of H_2 and $c-C_4H_4F_4$ in the presence of mercury vapor. In the photolysis of a mixture of 400 Torr of hydrogen and 20 Torr of $c-C_4H_4F_4$ essentially all the excited mercury atoms will be quenched by hydrogen since its quenching cross section (8.6 \AA^2 [12]) and relative concentration are each 20 times larger than those of $c-C_4H_4F_4$; thus only about one quenching event in 400 will involve the fluorocarbon directly:



(It is possible that this reaction proceeds via formation of HgH , although leading to the same final products.) Since $H\cdot$ atoms would be the only reactive species formed in the quenching process, all the products seen in the mixture of H_2 and $c-C_4H_4F_4$ must be due to the reactions of $H\cdot$ with $c-C_4H_4F_4$. Expected reactions of hydrogen atoms would be abstraction of $H\cdot$ from the substrate (probably with low yield), abstraction of $F\cdot$ from substrate and addition to substrate with ring opening (reactions (3), (4) and (5)). Production of H_2 in reaction (3) cannot be observed directly owing to the presence of excess hydrogen. However, results from the pure system discussed above suggest that reaction (3) occurs with poor efficiency. This interpretation implies a small yield of $c-C_4H_3F_4\cdot$ in the mixtures, which is consistent with the small yields of the $C_6H_4F_6$ species under these conditions. Direct combination of C_4 radicals would not be expected in the mixture, consistent with the observation that C_8 products are not formed under these circumstances.

In summary, the behavior of 1,1,2,2-tetrafluorocyclobutane in mercury sensitized photolysis experiments is consistent with expectations from the work of Scott and Jennings as regards low efficiency in the chemical quenching process and low efficiency of hydrogen atom attack on substrate. The predominant subsequent reaction seen by Scott and Jennings, namely recombination of $H\cdot$ with a fluoroalkyl radical followed by HF elimination, also contributes to some extent in the present system. However, owing to the considerable ring strain in $c-C_4H_4F_4$, other reactions are more prominent including $F\cdot$ atom abstraction, ring opening and rupture into two C_2 fragments or C_1 and C_3 products. As in other systems, the primary chemical quenching act is rupture of a C—H bond, as shown by formation of $c-C_4H_3F_4I$ in the presence of added iodine.

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