THE GAS PHASE PHOTOLYSIS OF PENTAFLUOROPYRIDINE

EMIL RATAJCZAK and BARBARA SZTUBA

Department of Physical Chemistry, Institute of Chemistry and Physics, Medical Academy, 50-140 Wrocław (Poland)

DENNIS PRICE

University of Salford, Department of Chemistry and Applied Chemistry, Salford, M5 4WT (Gt. Britain)

Summary

Continuous photolysis of pentafluoropyridine produced the Dewar isomer which underwent rearomatization with a half-life of about 5 days at room temperature. Flash photolysis of pentafluoropyridine gave two transients which decayed with half-lives of 22 ms and 3 ms respectively. Evidence from UV absorption spectroscopy and mass spectrometry indicated that these intermediates were the two isomers of fulvene. The possible reaction pathways involved in the photoisomerization processes of pentafluoropyridine are discussed.

1. Introduction

During the past decade a great deal of attention has been focused on valence-bond isomers of aromatic molecules and this topic has been frequently reviewed [1 - 5]. Photoisomerization of the hexafluorobenzene molecule to its Dewar isomer has been studied by Camaggi *et al.* [6] and Haller [7, 8]. Theoretical and experimental data [4, 7 - 10] suggest that photochemical transformation of hexafluorobenzene into the Dewar isomer is a symmetry-allowed process occurring from the S_2 or the S_3 singlet state.

Identification of Dewar pyridine in the products of the photolysis of pyridine [11] and the first synthesis of derivatives of Dewar pyridine and azaprismane [12] have prompted further investigation of valence-bond isomers of heterocyclic aromatic systems. Dewar isomers have previously been identified as the photolysis products of perfluoroalkyl [12, 13] and alkyl-fluorinated [14 - 16] derivatives of pyridine. Therefore it is reasonable to expect that photoisomerization of pyridine compounds into the corresponding valence isomers is a prevailing phenomenon. Since the valence-bond isomers of fluorinated aromatic compounds are generally more stable than

non-fluorinated isomers, we extended the range of such compounds studied by investigating the gas phase photolysis of pentafluoropyridine (PFP). The results of these experiments are reported in this work.

2. Experimental

The method of continuous photolysis was essentially the same as that described elsewhere [17]. PFP in the vapour phase was irradiated, using a 125 W medium pressure mercury arc lamp, in quartz vessels (volumes of 0.7 and 2.6 dm^3) for 4 - 74 h. The products of the photolysis were analysed by gas chromatography using two consecutive columns, a 2 m $\times$ 4 mm column packed with 60 - 80 mesh Chromosorb W impregnated with 15 wt.% of dinonyl phthalate followed by a 4 m $\times$ 4 mm column packed with 60 - 80 mesh Sterchamol impregnated with 35 wt.% of Carbowax 1500. Areas under the chromatographic peaks were measured with a planimeter; only their ratios were used.

The ^{13}C nuclear magnetic resonance (NMR) spectrum of the single photolysis product isolated was obtained at 25.2 MHz on a Jeol-INM-PFT-100 spectrometer operating in the pulsed Fourier transform mode, with deuterated chloroform being used as the solvent/internal standard.

The flash photospectroscopic study was performed using conventional equipment [18] and the experimental arrangement used has been discussed elsewhere [19]. Experiments were performed on two sets of apparatus, one at Salford and the other in Poland. Identical results were obtained on each. PFP was flash photolysed at room temperature in a cylindrical quartz vessel, 245 mm long and of internal diameter 12 mm. Details of the experimental conditions are given in Table 1. The photolysis flash discharged 980 J in the wavelength region 200 - 400 nm in approximately 30 μs. The spectroscopic flash lamp, 60 J and of 30 μs duration, was timed to fire at a predetermined interval after the photolysis flash. A series of experiments enabled the absorption spectrum of the reaction mixture to be photographically recorded at

TABLE 1

Conditions of PFP flash photospectroscopy experiments[a]

Composition of reaction mixture	Delay times
x_{PFP} = 0.03; x_{Ar} = 0.97	150 μs, 400 μs, 1 ms, 5 ms, 10 ms, 100 ms, 120 s
x_{PFP} = 0.20; x_{Ar} = 0.80	150 μs, 400 μs, 1 ms, 60 s
x_{PFP} = 0.40; x_{Ar} = 0.60	150 μs, 400 μs, 1 ms, 5 ms, 10 ms, 100 ms, 120 s

[a]For a total pressure of 2700 N m^{-2}.

various reaction time intervals; thus the presence of transients could be detected and values of the rate constants for their decay determined. The photographic plates were analysed using either a Carl—Zeiss—Jena GII or a Joyce—Loebl microdensitometer.

The flash photolysis of PFP was also investigated using time-resolved mass spectrometry. The experimental technique has been detailed elsewhere [20]. A 4:1 PFP—Ar mixture at a total pressure of 200 N m^{-2} was exposed to a 1400 J photoflash of 30 μs duration in the wavelength region 200 - 490 nm.

The PFP was obtained from Fluorochem Ltd. and was found to be chromatographically pure. All manipulations were performed on a conventional high vacuum line.

3. Results and discussion

3.1. Continuous photolysis

Continuous photolysis of PFP yielded a mixture of six products which were separated and were then analysed using ^{13}C NMR spectroscopy. Only in the case of one product was the yield (approximately 1%) sufficient for the ^{13}C spectrum to be obtained and for a Dewar isomer structure to be assigned. The ^{13}C NMR spectrum of the identified isomer showed the following bands (ppm): +202, +194, +184, +156, +120, +53, +26, —1, —5, —11 and —177. The bands +156 and +120 ppm indicate the presence of double bonds in the Dewar structure. However, because of the low concentration of sample analysed, only weak signals close to the noise level were recorded and interpretation of the spectrum is ambiguous. CNDO/2 calculations of the minimum electron energy for the two possible structures for Dewar pyridine indicated that the structure shown in Fig. 1 would be the more thermodynamically stable [21].

Apart from the technical difficulties of chromatographic separation of the product mixture, the main problem lay in obtaining sufficient sample for spectroscopic studies. Thus, in order to collect the identified sample of Dewar isomer, about 400 photolysis experiments had to be carried out. It should be noted that, apart from this main product, one other thermally aromatizing compound was observed but not in a sufficient amount for identification.

Additional experiments showed that the PFP Dewar isomer in PFP solution undergoes rearomatization with a reaction half-life of about 5 days at room temperature. This thermal instability, coupled with the long tedious preparation required to obtain a sample of pure PFP Dewar isomer, makes
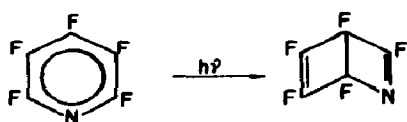

Fig. 1. The structures of PFP and Dewar PFP.

an exhaustive kinetic investigation of the isomerization using conventional static methods impractical.

3.2. Flash photolysis

Typical absorption spectra in the regions 225 - 270 and 270 - 300 nm obtained following the flash photolysis of PFP are given in Fig. 2. These show that, 150 μs after the photolysis flash, absorption bands due to transient species overlay those of PFP. The intensity of these new bands decreases as the reaction time increases, disappearing completely a few seconds after the photoflash. In Fig. 3 microdensitometer traces of the absorption spectrum, taken before and 40 s after the photoflash (curve 1) and 150 μs (curve 2) after the photoflash, are given. In the region 230 - 265 nm a decrease in absorption compared with the PFP absorption is observed, whereas in the region 265 - 285 nm an increase is observed. As the delay of reaction time is increased the absorption spectrum of the reaction mixture returns gradually to that of the original PFP (Figs. 2 and 3).

Kinetic analysis of the rate of change of the absorption spectra [18] showed that the transient decay is first order. The rate constants for decay of the transients produced by the flash photolysis of PFP were found from the slopes of the first order plots shown in Fig. 4 to be

$$k_I = 32.0 \pm 1.6 \text{ s}^{-1} \quad \text{in the range 230 - 265 nm}$$
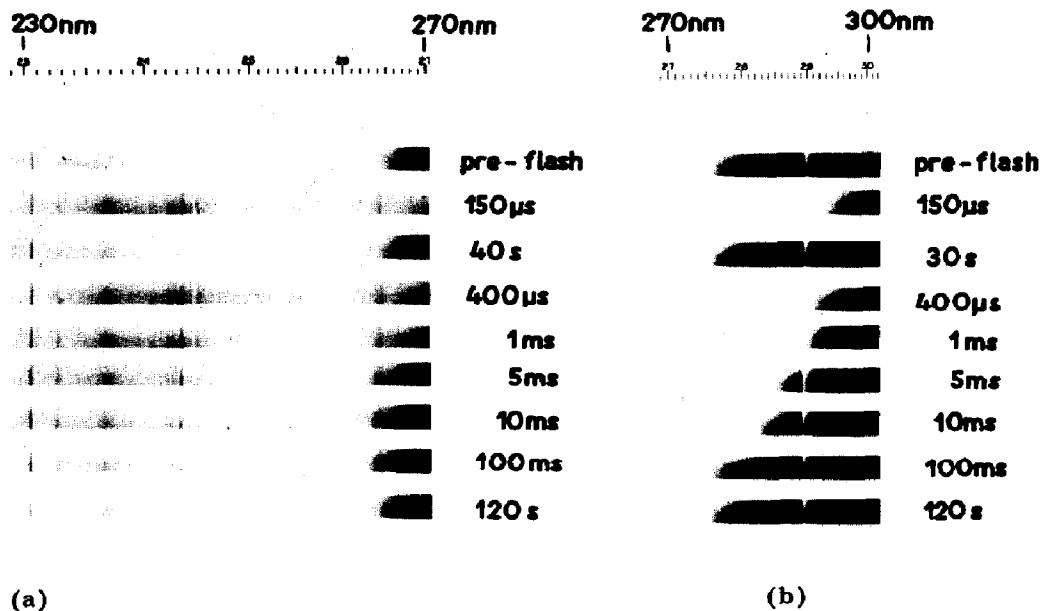$$k_{II} = 221 \pm 8 \text{ s}^{-1} \quad \text{in the range 265 - 285 nm}$$

(a)

(b)

Fig. 2. Absorption spectra obtained for the flash photolysis of PFP at a total pressure of 2700 N m^{-2}: (a) x_{PFP} = 0.03, x_{Ar} = 0.97; (b) x_{PFP} = 0.40, x_{Ar} = 0.60.
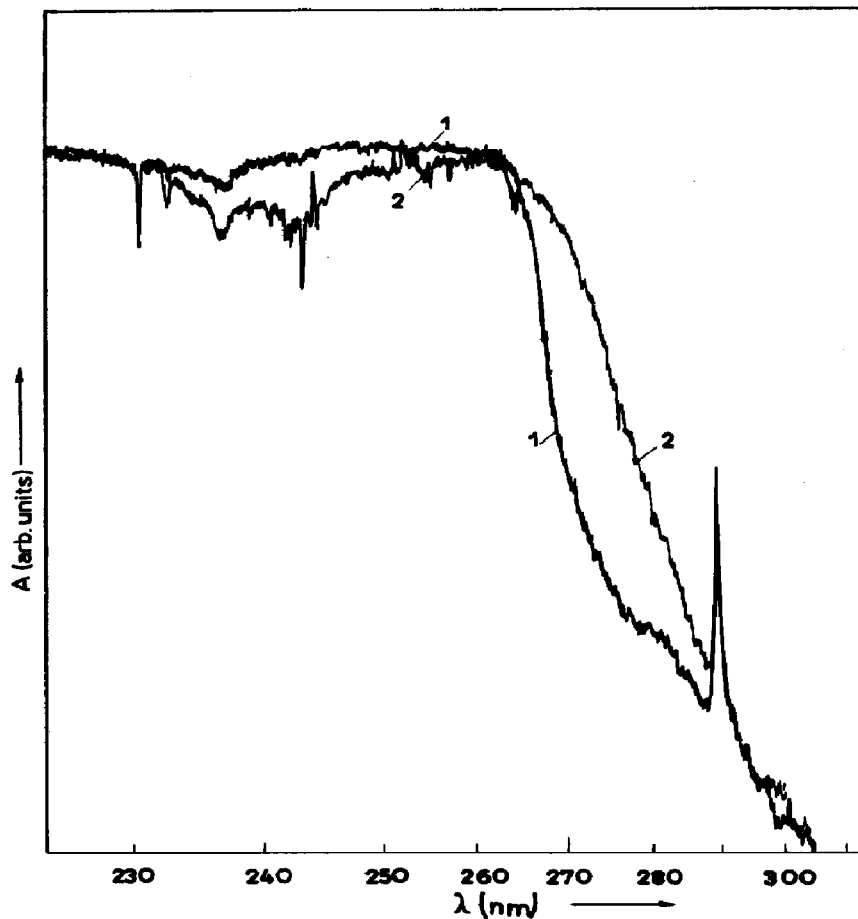
Fig. 3. Typical microdensitometer traces of the absorption spectrum with $x_{PFP} = 0.03$, $x_{Ar} = 0.97$ and at a total pressure of 2700 N m^{-2}: 1, before the photoflash and 40 s after the photoflash; 2, 150 μs after the photoflash.
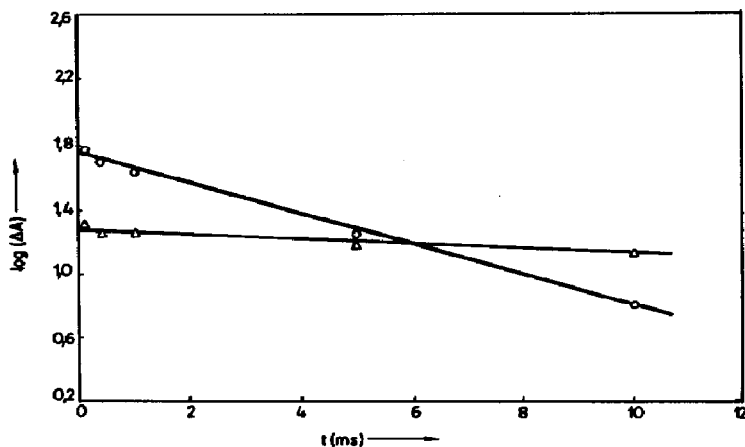

Fig. 4. First order decay plots for $x_{PFP} = 0.03$, $x_{Ar} = 0.97$ and at a total pressure of 2700 N m^{-2} for the transients detected at 245 nm ($\triangle$, $k = 32 \pm 1.56$ s^{-1}) and 270 nm ($\bigcirc$, $k = 221 \pm 8$ s^{-1}).

The significant difference in the values of these rate constants suggests that two transients, one absorbing in the region 230 - 265 nm and the other absorbing in the region 265 - 285 nm, are produced by the flash photolysis of PFP. Both transients disappear within a few seconds after the photoflash, reverting to PFP. In another experiment it was found that the values of the rate constants k_I and k_{II} do not depend on the presence of oxygen in the flash photolysis system. No stable photoproducts were detected in any of these experiments.

The half-lives of these transients were calculated to be τ_I = 22 ms and τ_{II} = 3 ms; the relatively high values suggest that these intermediates are not free radical in nature. It is probable that the half-life for the decay of triplet PFP is less than that for the decay of triplet benzene which is reported to be in the range 10 - 50 μs [22, 23]; the decay half-lives of singlet states of simple aromatic molecules are of the order of nanoseconds [24, 25]. Thus our experimental data suggest that the transients produced via the flash photolysis of PFP are not electronically excited states of the parent molecules. The relative stability of the PFP flash photolysis products and their complete reversion to PFP indicates that, following flash photolysis of PFP, unstable photoisomers are produced.

We have recently reported briefly some preliminary studies on the flash photolysis of PFP using a time-of-flight mass spectrometer to monitor the subsequent reaction [20, 26]. In Fig. 5 the mass spectrum obtained 300 μs after the photoflash is compared with the spectra obtained before the photoflash and 10 s after the photoflash. The significant difference observed is the appearance, 300 μs after the photoflash, of new peaks at m/e 45 (NCF$^+$) and at m/e 50 (CF$_2^+$). The CF$_2^+$ ion could only result from the fragmentation of an ionized fulvene structure, indicating that this is the structure type of the intermediate produced via the flash photolysis of PFP. It is probable that the two possible isomers of fulvene have very similar mass spectra [27] which could not be distinguished with the low resolution mass spectrometer used. The presence of both could be detected by the much more sensitive absorption spectroscopy but the latter only indicates the presence of dienes absorbing in the given wavelength range.

The temporal behaviour of the CF$_2^+$ signal, and hence of the transient from which it is derived, is shown in Fig. 6. The species increases to a maximum after 300 μs and then decays. The decay was found to obey first order kinetics with a rate constant value of 610 ± 100 s^{-1}. If the influence of the initial adiabatic heating, which inevitably occurs during the mass spectrometry experiments, is taken into account, this value for the rate constant is not unreasonable when compared with those given previously for the spectroscopic experiments. The extent of adiabatic heating in flash-photolysed gaseous systems can be estimated using an equation of the Meyer type [28] in which the resultant temperature rise is determined as the ratio of the energy released to the total heat capacity of the gaseous system. Thus it is possible to minimize the effect by the use of high dilution with an inert gas. In the flash spectroscopic studies performed in this work the dilution of PFP
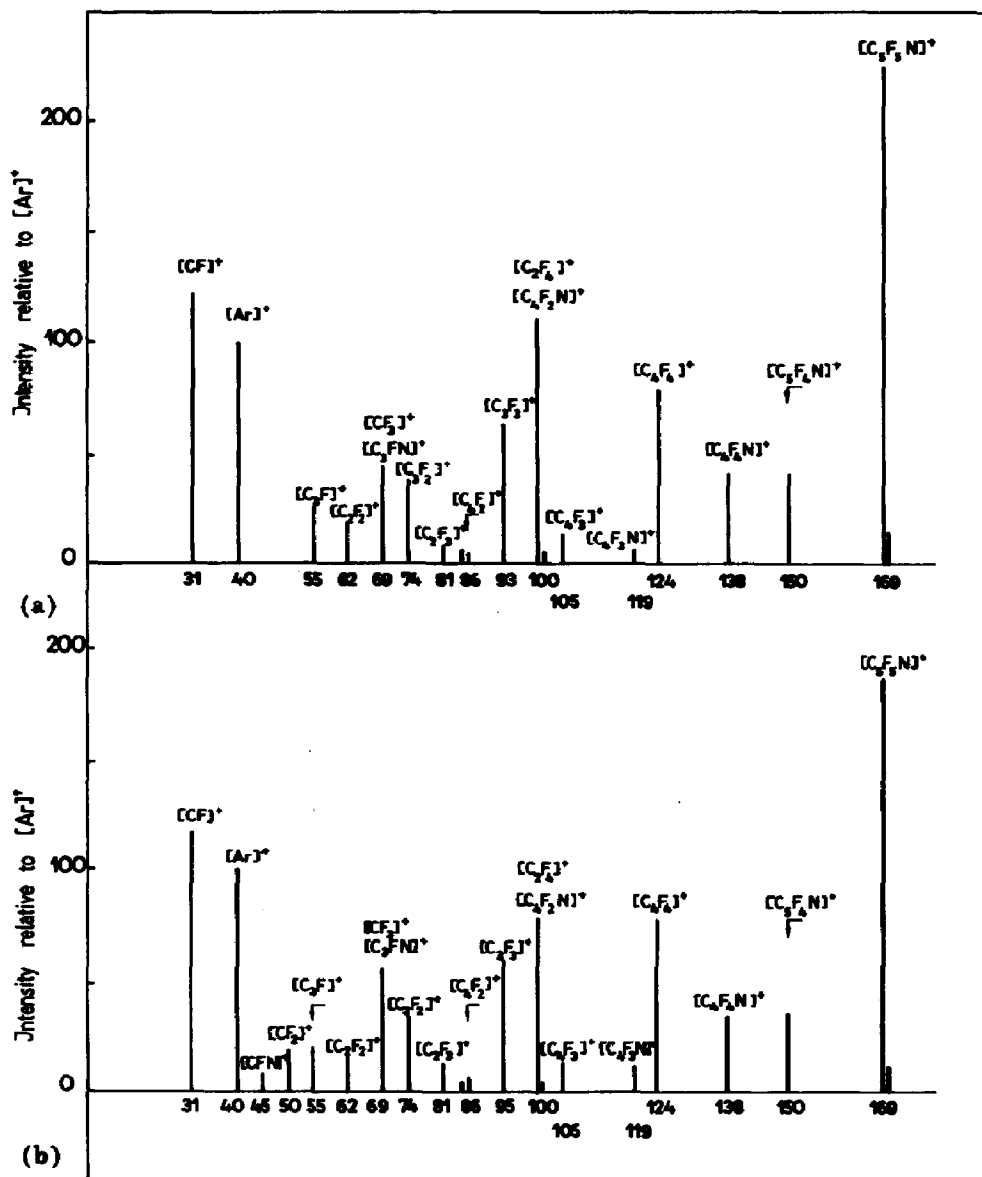
Fig. 5. Mass spectra (at 70 eV) showing the production of a transient via the flash photolysis of PFP: (a) before the flash and 10 s after the flash; (b) 300 μs after flash. PFP:Ar = 4:1 at a total pressure of 200 N m^{-2}.

with argon was in excess of 20-fold so that any temperature rise could be ignored, *i.e.* the rate constants for the photoisomer decay were determined at room temperature. In the mass spectrometry experiment it is not possible to remove the effect of adiabatic heating by dilution [29]. This limitation arises from the requirement to work at low pressures to avoid saturating the mass spectrometer and at low dilution to obtain measurable concentration
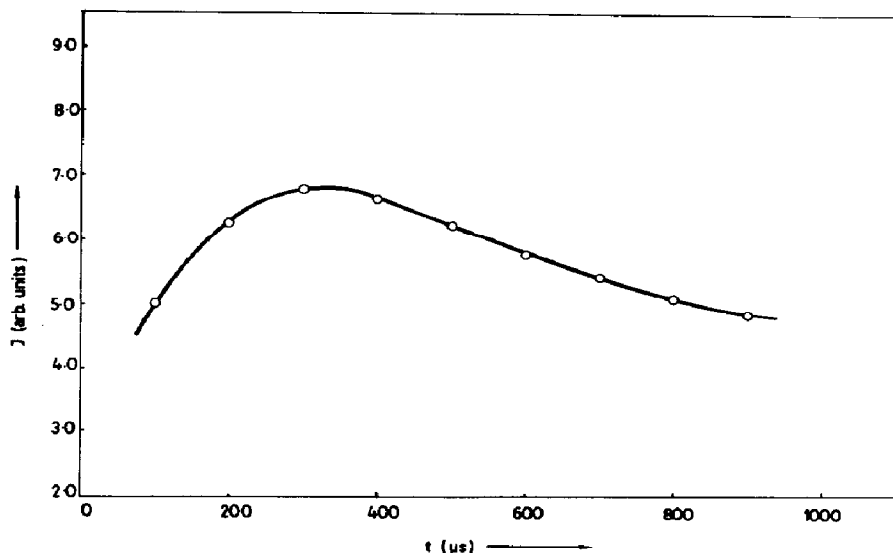
Fig. 6. The temporal behaviour of the transient produced by the flash photolysis of PFP as shown by the relative intensity J of the CF_2^+ ion peak. PFP:Ar = 4:1 at a total pressure of 200 N m^{-2}.

changes. Because the PFP:Ar ratio was 4:1 in the reported experiments, the temperature effect should not be ignored and could easily account for the threefold difference between the rate constants obtained by the two methods.

The absorption spectra given in Fig. 2 indicate that the flash photolysis of PFP yields two unstable photoisomers which are shown by mass spectrometry to have a fulvene structure. In the case of PFP two fulvene structures are possible (see Fig. 7). Unsubstituted fulvene is known to be unstable and

Fig. 7. The two possible fulvene structures.

as yet has not been isolated [4]. The instability of the PFP fulvene photoisomers is greater than that of unsubstituted fulvene, presumably because of destabilization of olefinic bonds following fluorine substitutions. Our experimental data indicate that perfluorinated fulvene structures are subject to rearomatization. The photochemical rearomatization of fulvene has been observed [30] but not in the case of the analogous aromatic perfluorinated systems.

The valence isomerization of PFP observed in both the continuous and flash photolysis experiments probably occurs according to the model pro-

posed for the valence photoisomerization of alkylbenzenes [4]. After flash photolysis two fulvene structures result from a PFP transient which may, by analogy to the photoisomerization of benzvalene to fulvene [31, 32], have a benzvalene structure. Under continuous photolysis this transient is rearranged into two possible Dewar structures.

The tendency for *para*-bonding which is apparent in fluorobenzenes has also been observed in the PFP molecule. According to the mechanism proposed for the photoisomerization of benzene and its derivatives, Dewar benzene can be formed from either the S_2 or the S_3 singlet state [4]. Our results exclude the presence of a triplet state during the valence isomerization of PFP to Dewar PFP. The formation of two unstable PFP photoisomers with half-lives of 22 ms and 3 ms indicates that one other intermediate is formed and that the direct formation of the fulvene isomer from the singlet state of PFP is unlikely. Similarly, direct formation of the Dewar isomer from singlet-state PFP in continuous photolysis is not considered to be possible. Theoretical studies concerned with benzene photoisomerization suggest that pre-fulvene is the precursor of fulvene and benzvalene [4, 33]. Benzvalene is formed from the singlet state of benzene after a time within the range of nanoseconds in a two-step process via intramolecular cyclization of pre-fulvene. Formation of fulvene isomers and Dewar PFP is probably the final step of the PFP photoisomerization in the gas phase (Fig. 8). These processes, which have been investigated in our studies, occur after a time within the range of microseconds. Isomerization of benzvalene to fulvene and to benzene is sensitized by triplet benzene [34]. In the flash photolysis of PFP high concentrations of electronically excited molecules in both singlet and triplet states will be formed; therefore under these conditions the formation of the fulvene isomer is a dominant and highly efficient process. In continuous photolysis the dominant process will be the change of the photostationary state towards the formation of thermodynamically more stable products.
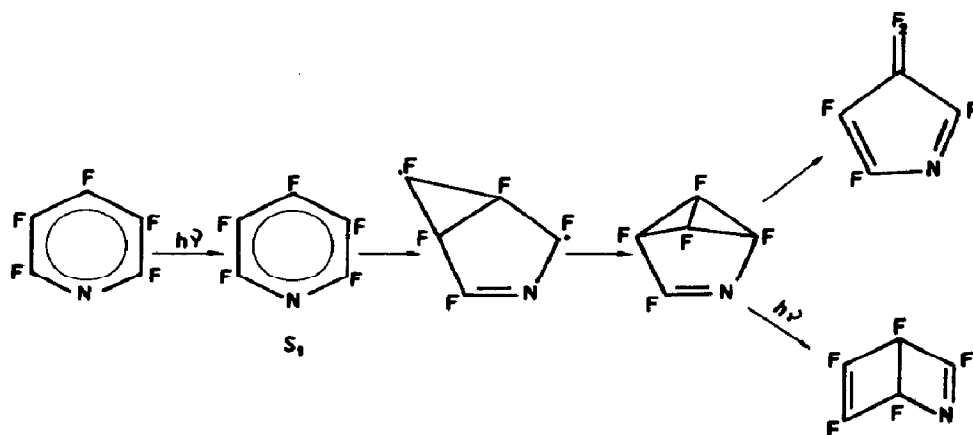

Fig. 8. Possible reaction pathways following the photolysis of PFP.

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Acknowledgments

References

1 *Photochemistry — Specialist Periodical Reports*, Vols. 1 - 8, The Chemical Society, London, 1970 - 1977.
2 L. T. Scott and M. Jones, Jr., *Chem. Rev., 72* (1972) 181.
3 W. A. Noyes and K. E. Al-Ani, Jr., *Chem. Rev., 74* (1974) 29.
4 D. Bryce-Smith and A. Gilbert, *Tetrahedron, 32* (1976) 1309.
5 M. Zupan and B. Sket, *Isr. J. Chem., 17* (1978) 92.
6 G. Camaggi, F. Gozzo and G. Cevidalli, *Chem. Commun.*, (1966) 313.
7 I. Haller, *J. Am. Chem. Soc., 88* (1966) 2070.
8 I. Haller, *J. Chem. Phys., 47* (1967) 1117.
9 D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, (1966) 593.
10 D. Phillips, *J. Chem. Phys., 46* (1967) 4679.
11 K. E. Wilzbach and D. J. Rausch, *J. Am. Chem. Soc., 92* (1970) 2178.
12 M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *Chem. Commun.*, (1970) 1580.
13 M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans I*, (1973) 1542.
14 Y. Kobayashi, A. Ohsawa, M. Baba, T. Sato and I. Kumadaki, *Chem. Pharm. Bull., 24* (1976) 2219.
15 S. Caplain and C. A. Lablache, *Chem. Commun.*, (1970) 1247.
16 S. Caplain, J. P. Catteau and C. A. Lablache, *Chem. Commun.*, (1970) 1475.
17 E. Ratajczak, *Rocz. Chem., 44* (1970) 447.
18 G. Porter and M. A. West, in G. G. Hammes (ed.), *Investigation of Rates and Mechanisms of Reactions*, Wiley, New York, 3rd edn., 1974, Part II, Chap. X.
19 J. H. Allen and J. F. McKellar, *Lab. Pract., 16* (1967) 991.
20 D. Price and E. Ratajczak, in D. Price and J. F. J. Todd (eds.), *Dynamic Mass Spectrometry*, Vol. 5, Heyden, London, 1978 p. 176.
21 Z. Latajka, H. Ratajczak, W. J. Orville-Thomas and E. Ratajczak, *J. Mol. Struct., 21* (1974) 299.
22 R. B. Cundall and A. S. Davies, *Trans. Faraday. Soc., 62* (1966) 1151.
23 C. S. Parmenter and B. L. Ring, *J. Chem. Phys., 46* (1967) 1998.
24 J. P. Simons, *Fotochemia i spektroskopia*, PWN, Warsaw, 1976; *Photochemistry and Spectroscopy*, Wiley—Interscience, London, 1971.
25 R. B. Cundall and A. Gilbert, *Studies in Modern Chemistry, Photochemistry*, Nelson, London, 1970.
26 D. Price and E. Ratajczak, *Chem. Commun.*, (1976) 902.
27 M-Th. Pract., M-J. Hubin-Franskin, J. P. Delwiche and R. Schoos, *Org. Mass Spectrom., 12* (1977) 297.
28 R. T. Meyer, *J. Sci. Instrum., 44* (1968) 422.
29 D. Price and E. Ratajczak, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., 27* (1979) 195.
30 L. Kaplan, S. P. Walch and K. E. Wilzbach, *J. Am. Chem. Soc., 90* (1968) 5646.
31 K. E. Wilzbach, J. S. Ritscher and L. Kaplan, *J. Am. Chem. Soc., 89* (1967) 1031.
32 L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc., 90* (1968) 3291.
33 I. Jano and Y. Mori, *Chem. Phys. Lett., 2* (1968) 185.
34 A. Cox and T. J. Kemp, *Introductory Photochemistry*, McGraw-Hill, London, 1971, Chap. 4.