Detection of a Transient after Flash Photolysis of the Aromatic Molecules C_6X_6 (X = H, D, F) and C_5Y_5N (Y = H, F) in the Gas Phase

By D. Price*
(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT)
and E. Ratajczak
(*Institute of Chemistry and Technology of Medicinal Products, Medical Academy,* 50–140 *Wroclaw, Poland*)

Summary Flash photolysis of the aromatic molecules C_6H_6, C_6D_6, C_6F_6, C_5H_5N, and C_5F_5N, in the gas phase, yields a transient which decays completely back to the original species after a few seconds; values of the rate constants for this decay are given.

We report the observation of a short-lived, non-electronically excited transient following the gas-phase flash photolysis of benzene, hexadeuteriobenzene, hexafluorobenzene, pyridine, and pentafluoropyridine diluted with argon. The flash lamp used emitted *ca.* 10^{18} quanta per flash in the wavelength region 200–490 nm.[1] Time-of-flight mass spectrometry[2] and absorption spectrophotometry[3] were used as monitoring techniques. Both methods detected the formation of intermediates with lifetimes greater than 1 ms in these systems. The decrease in molecular ion intensity indicated that some 40% of the aromatic molecules were converted into transients at times between 100 and 300 μs after the flash.

In all systems studied new mass spectral peaks were detected immediately after the flash and also changes were observed in the intensities of some of the original peaks. These changes must have been due to the formation of a new species in the reaction system. Initially the intensities of the new peaks, and hence the transient concentration, increased to a maximum after which there was a gradual decay to zero. In the case of C_6F_6, the production of a transient was confirmed by the detection of new mass spectral peaks in experiments performed with the mass spectrometer operating at low electron energies (11 eV). Under these conditions the $C_6F_6^+$ ion is the only one due to the parent molecule. No change in the extent of formation of the transient or its kinetic behaviour was observed when oxygen was added to the C_6F_6 system or when the total pressure of this system was reduced from 200 to 50 N m^{-2}. All systems reverted cleanly to their original composition a few seconds after the flash. A first-order plot using the final decay portion of transient concentration *vs.* time profiles yields the rate constant (k) for the decay of the transient species. The values of the rate constants obtained and details of the new peaks observed are collated in the Table.

The behaviour observed by mass spectrometry was confirmed in the cases of C_6F_6 and C_5F_5N by experiments using the conventional flash spectroscopic technique. The transients produced resulted in increased absorption in the region 255–285 nm in the case of C_6F_6 and at the wavelength of maximum absorption, namely 285 nm, for C_5F_5N. In both cases the kinetic behaviour was similar to that observed by mass spectrometry.

The mass spectrometric and spectroscopic data provide clear evidence that a transient is formed after the flash photolysis of these aromatic compounds. Since the transient lifetimes are greater than 1 ms it is unlikely that they are electronically excited states of the parent species. The lack of effect of adding oxygen to the C_6F_6 system plus the relatively long reaction times suggest that the intermediate is not free radical in nature. For benzene, hexadeuteriobenzene, and pyridine, the post-flash mass spectra suggest that the intermediate may have a prismane[4] type of structure. This seems to be in agreement with the post-flash u.v. spectra as in the case of benzene only the much shorter-lived triplet benzene could be detected using absorption spectroscopy.[5] The perfluorinated compounds produced more complicated mass spectra and it is not possible to reach a conclusive assignment of the structure of their intermediate at this stage although the evidence does favour a fulvene[4] type structure.

TABLE. Mass spectrometric observations following the flash photolysis of aromatic molecules (aromatic molecule:argon = 4:1; total pressure = 200 N m^{-2}; flash energy = 1400 J).

	Post flash			
Aromatic molecule	New peaks m/e	Probable ion formulae	Period decay observed/ms	$k \times 10^{-2}$ s^{-1}
C_6H_6	26	$C_2H_2^+$	1·1–3·5	1·4 ± 0·2
C_6D_6	28	$C_2D_2^+$	1·2–3·0	0·85 ± 0·2
C_6F_6	50	CF_2^+	0·2–1·0	18 ± 2·0
	81	$C_2F_3^+$		
	86	$C_4F_2^+$		
	100	$C_2F_4^+$		
	136	$C_5F_4^+$		
C_5H_5N	25	C_2H^+	0·8–2·0	3·6 ± 0·3
	26	$C_2H_2^+$ and/or CN^+		
	27	$C_2H_3^+$ and/or HCN^+		
	28	$C_2H_4^+$ and/or H_2CN^+		
C_5F_5N	45	FCN^+	0·4–0·9	6·1 ± 1·0
	50	CF_2^+		

(*Received*, 30*th July* 1976; *Com.* 877.)

---

[1] D. R. A. Cuff, D. Price, and R. Whitehead, *J. Photochem.*, 1974, **3**, 215.

[2] S. B. Howarth, J. H. Lippiatt, D. Price, G. B. Ward, and P. Myers, *Internat. J. Mass. Spectrom. Ion Phys.*, 1972, **9**, 95; D. Price and E. Ratajczak, *Bull. Acad. Polon. Sci., Ser. Sci. chim.*, submitted for publication.

[3] J. H. Allen and J. F. McKellar, *Lab. Practice*, 1967, **16**, 991.

[4] L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 1972, **72**, 181.

[5] T. S. Godfrey and G. Parker, *Trans. Faraday Soc.*, 1966, **62**, 7; C. S. Parmenter, *Adv. Chem. Phys.*, 1972, XXII, 365.