

THE GAS PHASE PHOTOLYSIS OF FURAN

DENNIS PRICE^a, EMIL RATAJCZAK^b, BARBARA SZTUBA^b and DARIUSZ SARZYNSKI^b

^aDepartment of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT (U.K.)

^bDepartment of Physical Chemistry, Medical Academy, 50-140 Wrocław (Poland)

(Received May 24, 1986; in revised form October 7, 1986)

Summary

Continuous photolysis of furan results in CO, C₂H₂, CO₂, propyne, 1-hexen-5-yne, 2,4- and 1,5-hexadiyne and an unidentified polymer. The identities of the products were determined by mass spectrometric analysis. Flash photolysis of furan gave a transient which decayed with a half-life of about 5 ms. Time-of-flight mass spectrometric analysis indicated that this intermediate was Dewar furan. The possible reaction pathways involved in the photolysis of furan are discussed.

1. Introduction

The photochemistry of five-membered heterocyclic ring systems has attracted great interest in recent years. The wide diversity of transformations that heterocyclic compounds undergo on electronic excitation has been the subject of earlier reviews [1 - 3]. There have been numerous investigations of the mechanisms to account for the photorearrangements of all five-membered heteroaromatic compounds. In particular the behaviour of valence bond isomers and their intermediacy in these photorearrangements has received much attention. Substituted Dewar isomers of pyridines [4, 5], pyridazines [6, 7], pyrroles [8, 9] and thiophenes [10 - 12] have been obtained by photolysis. Except for Dewar pyridine [13] and Dewar thiophene [14] no parent Dewar isomers of the heteroaromatics have been reported.

The first substituted Dewar furan was synthesized by Wirth and Lemal [15]. Pitt *et al.* [16] have recently reported the generation of Dewar furan and its trapping with isobenzofuran. Dewar and valene structures of the furan molecule have been subjected to *ab initio* and CNDO/2 molecular orbital calculations [17]. Predicted geometrical parameters agree favourably with experimental values for Dewar benzene and benzvalene.

We now wish to report the observation that the gas phase photolysis of furan vapour leads to a transient isomer of the Dewar type.

2. Experimental details

The flash photolysis of furan was investigated using a time-of-flight mass spectrometer and the experimental arrangement used has been discussed elsewhere [18]. The reaction vessel contained a 50% mixture of furan in krypton at a total pressure of 200 N m^{-2} . The flash lamp used discharged 1400 J in $30 \mu\text{s}$, emitting about 10^{18} quanta in the wavelength region $200 - 490 \text{ nm}$. A time-of-flight mass spectrometer was used to obtain mass spectra of the reacting system at intervals of $60 \mu\text{s}$.

The method of continuous photolysis has been described elsewhere [19]. Saturated furan vapour was irradiated in a quartz vessel (2 dm^3) using 400 W Zn-Cd resonance lamps for 1 - 6 h. The photolysis products were separated and analysed by gas chromatography using a katharometer as detector and a $3 \text{ m} \times 4 \text{ mm}$ column packed with 60 - 80 mesh Chromosorb W impregnated with 15 wt.% dinonyl phthalate. The column was operated at 300 K . The mass spectra of the isolated products were recorded with a Joel JMS-D 100 mass spectrometer operating at 75 eV .

Furan was obtained from Koch-Light Laboratories Ltd. and was found to be chromatographically pure after degassing and bulb-to-bulb distillation.

3. Results and discussion

Following the flash photolysis of furan transient mass spectra were observed to be superimposed on those of the parent species. Changes in the mass spectral cracking pattern can be seen from Table 1 and Fig. 1 where the mass spectrum of the reaction mixture at $200 \mu\text{s}$ after the flash is compared with the identical spectra taken before and 1 s after the flash. New peaks at m/z values of 49 (C_4H^+), 50 (C_4H_2^+), 51 (C_4H_3^+) and 52 (C_4H_4^+) were observed while a significant relative intensity increase (from 11 to 49) at $m/z = 26$ (C_2H_2^+) and (from 23 to 58) at $m/z = 28$ (C_2H_4^+) occurred with further increases at m/z values of 37 (C_3H^+), 38 (C_3H_2^+), 40 (C_3H_4^+ or C_2O^+) and 42 ($\text{C}_2\text{H}_2\text{O}^+$). The temporal behaviour of the C_4H_2^+ signal, and hence of the transient from which it is derived, is shown in Fig. 2. The species increases to a maximum after $200 \mu\text{s}$ and then gradually decays to zero. The half-life of this transient was calculated, on the assumption of first-order kinetics, to be about 5 ms. This relatively high value, together with the lack of any observed effect when oxygen was included in the system, suggests that the intermediate is neither free radical in nature nor an electronically excited state of the parent molecule. The C_4H^+ , C_4H_2^+ , C_4H_3^+ and C_4H_4^+ ions could only result from the fragmentation of an ionized Dewar structure, indicating that this is the structure type of the intermediate produced via the flash photolysis of furan.

TABLE 1

70 eV mass spectra before and after flash photolysis of furan^a

<i>m/z</i>	<i>Ion</i>	<i>Relative intensity</i>		
		<i>Before flash</i>	<i>200 μs after flash</i>	<i>1 s after flash</i>
12	C ⁺	4	4	4
16	O ⁺	8	8	8
26	C ₂ H ₂ ⁺	11	49	11
28	C ₂ H ₄ ⁺ and/or CO ⁺	23	58	26
29	CHO ⁺	22	22	17
37	C ₃ H ⁺	20	25	21
38	C ₃ H ₂ ⁺	27	31	26
39	C ₃ H ₃ ⁺	100	100	100
40	C ₃ H ₄ ⁺ and/or C ₂ O ⁺	29	45	40
42	C ₂ H ₂ O ⁺	25	28	22
49	C ₄ H ⁺	—	20	—
50	C ₄ H ₂ ⁺	—	33	—
51	C ₄ H ₃ ⁺	—	19	—
52	C ₄ H ₄ ⁺	—	20	—
68	C ₄ H ₄ O ⁺	92	82	97

^aKrypton used as internal standard in 1:1 furan:krypton mixture.

Since the initial adiabatic heating occurs during the flash photolysis mass spectrometry experiments, the Dewar furan formed could thermally rearrange into the parent molecule and/or to the cyclopropenyl carbonyl compound. Thus, a relative intensity increase of the parent ion C₄H₄O⁺ (from 82 to greater than 97) at 1 s after the flash in comparison with that of 200 μs after the flash could be attributed to the occurrence of Dewar isomer thermal rearrangement.

Continuous photolysis of furan vapour yielded a mixture of seven products: CO, CO₂, C₂H₂, C₃H₄, C₆H₈, two isomeric C₆H₆ and an unidentified polymer. The highest yields 30% - 50% for C₃H₄ formation and the lowest yields 0.5% - 3% for C₆H₈ formation were found relative to unconverted furan.

The structures of all compounds reported here were determined by analytical mass spectrometry. The mass spectra of four gaseous products separated from the reaction mixture contained the parent peaks at *m/z* 26, 28, 40 and 44 which were assigned to the presence of C₂H₂, CO, propyne and CO₂ respectively. More complex spectra were recorded for three other products, which were liquids at room temperature. Analysis of the spectral patterns resulted in the assignment of C₆H₈ and two C₆H₆ formulae. In the case of the C₆H₈ compound, the most intensive signals were observed at *m/z* 27 (C₂H₃⁺), 39 (C₃H₃⁺), 52 (C₄H₄⁺), 77 (C₆H₅⁺) and 79 (C₆H₇⁺) and indicated the structure of 1-hexen-5-yne. The two isomeric products of

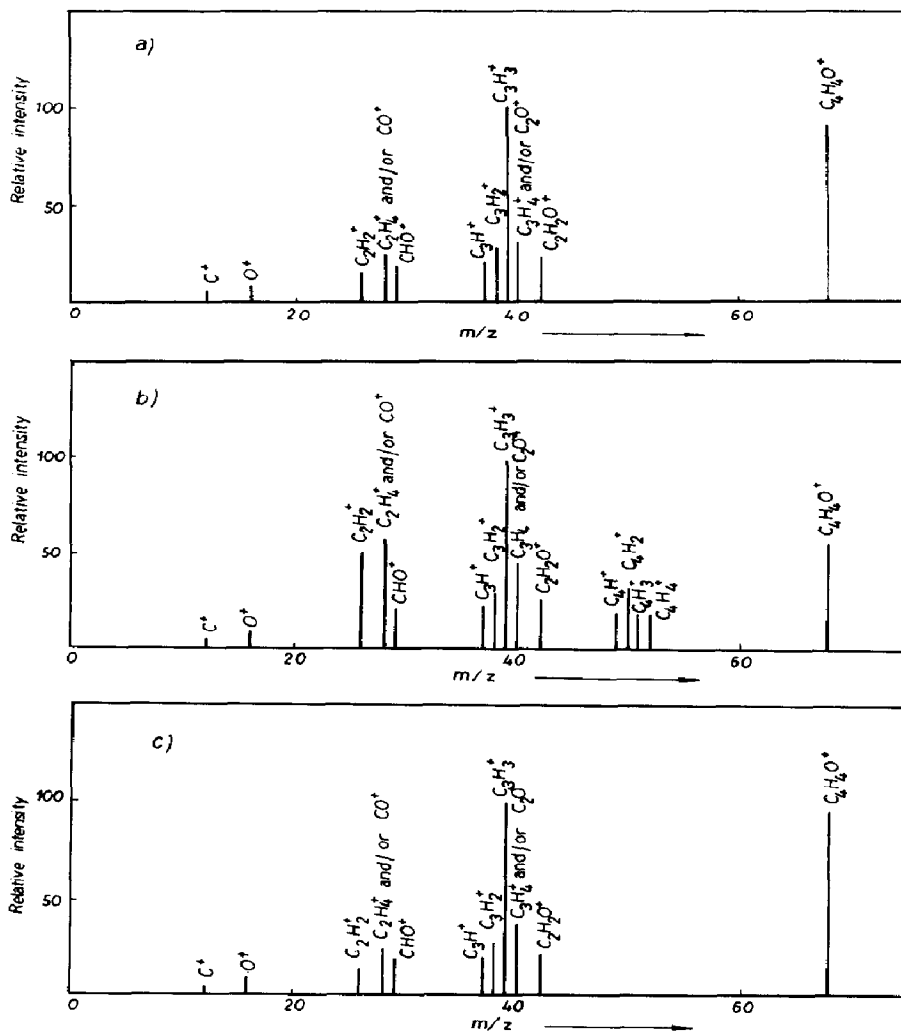


Fig. 1. 70 eV mass spectra showing the production of transient following the flash photolysis of furan: (a) pre-flash; (b) 200 μ s after the flash; (c) 1 s after the flash.

formula C_6H_6 were determined on the basis that their spectra contained the main signals at m/z 39 ($C_3H_3^+$), 50 ($C_4H_2^+$), 51 ($C_4H_3^+$), 52 ($C_4H_4^+$) and 77 ($C_6H_5^+$), and also by comparison with the spectra of the original compounds [20, 21].

The photorearrangement of furan I (Fig. 3) observed in both the flash and the continuous photolysis experiments probably occurs according to the mechanism proposed by Tamelen and Whitesides [22], involving C—O cleavage in the excited state to give a diradical intermediate II, followed by cyclopropenecarboxyaldehyde III formation. The intermediate cyclopropene is in equilibrium with a bicyclic isomer, Dewar furan IV. Dewar furan trapped in the liquid phase photolysis was found to convert

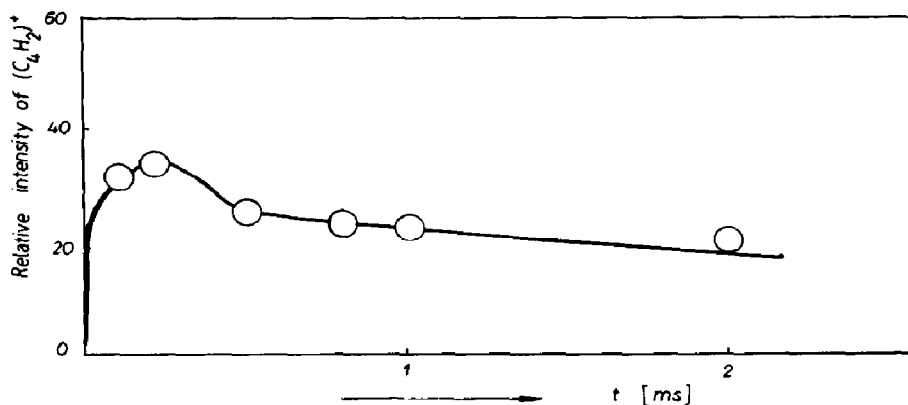


Fig. 2. Variation with time of the relative intensity of the $C_4H_2^+$ signal following the flash photolysis of the furan-krypton mixture.

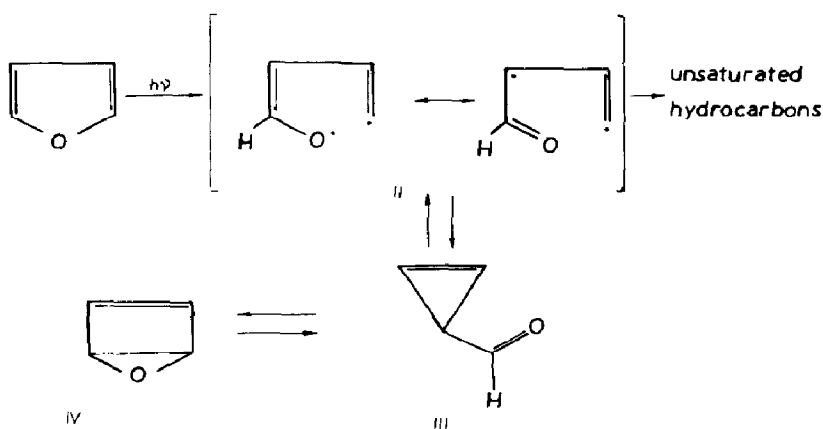


Fig. 3. Mechanistic possibilities for the photoisomerization of furan.

thermally to cyclopropenecarboxaldehyde III, but irradiation of III did not lead to furan formation [16]. Under the flash photolysis conditions the formation of the Dewar furan seems to be dominant and a highly efficient process, mainly owing to the high concentration of electronically excited molecules. In continuous photolysis a change in the photostationary state towards the competing process is observed. The formation of the unsaturated hydrocarbons C_2H_2 , C_6H_8 and C_6H_6 and the ring-contracted products C_3H_4 and CO at the diradical stage can be attributed to this competing process.

Difficulties in direct preparation and isolation of the unsubstituted heterocyclic Dewar isomers seem to be caused by their thermal instability. The half-life of Dewar furan (5 ms) is much shorter than that of Dewar benzene (2 days at 293 K) [23] and Dewar pyridine (2.5 min at 298 K) [13]. Since the valence bond isomers of fluorinated six-membered aromatic compounds are generally more stable than non-fluorinated isomers [4 - 7, 24 - 29] the same trend can be expected among five-membered heterocyclic

compounds. Indeed, the first isolations of the Dewar isomers of pyrrole [8], thiophene [10] and furan [15] were reported for their perfluorinated derivatives. The thermal stability of 2,3,4,5-tetrakis(trifluoromethyl)Dewar thiophene, which reverts to the parent compound with a half-life of 5.1 h in benzene at 433 K [30], is comparable with the thermal stability of the perfluoroalkyl pyridines [4] and pyridazines [6]. More experimental studies are required in order to find any further structure-reactivity correlations for the valence bond isomers of heterocyclic molecules.

Acknowledgments

The authors thank the Polish Academy of Science for support. E.R. wishes to thank the University of Salford for the award of a Visiting Lectureship.

References

- 1 A. Lablache-Combier and M. A. Remy, *Bull. Soc. Chim. Fr.*, (1971) 679.
- 2 S. Braslavsky and J. Heicklen, *Chem. Rev.*, 77 (1977) 473.
- 3 A. Padwa, in P. de Mayo (ed.), *Rearrangements in Ground and Excited States*, Vol. 3, pp. 502 - 547. In H. H. Wasserman (ed.), *Organic Chemistry*, Academic Press, New York, 1980.
- 4 M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *J. Chem. Soc., Perkin Trans. I*, (1973) 1542.
- 5 E. Ratajczak, B. Sztuba and D. Price, *J. Photochem.*, 13 (1980) 233.
- 6 R. D. Chambers, W. K. R. Musgrave and K. C. Srivastava, *J. Chem. Soc., Chem. Commun.*, (1971) 264.
- 7 R. D. Chambers, J. R. Maslakiewicz and K. C. Srivastava, *J. Chem. Soc., Perkin Trans. I*, (1975) 1130.
- 8 H. J. Hiraoka, *J. Chem. Soc., Chem. Commun.*, (1971) 1610.
- 9 J. A. Baltrop, A. C. Day and R. R. Ward, *J. Chem. Soc., Chem. Commun.*, (1978) 131.
- 10 H. A. Wiebe, S. Braslavsky and J. Heicklen, *Can. J. Chem.*, 50 (1972) 2721.
- 11 Y. Kobayashi, I. Kumadaki, A. Oshawa, Y. Sekine and H. Mochizuki, *Chem. Pharmacol., Bull.*, 23 (1975) 2773.
- 12 Y. Kobayashi, K. Kawade, A. Ando and I. Kumadaki, *Heterocycles*, 20 (1983) 174.
- 13 K. E. Wilzbach and D. J. Rausch, *J. Am. Chem. Soc.*, 92 (1970) 2178.
- 14 W. A. Rendall, M. Torres and O. P. Strausz, *J. Am. Chem. Soc.*, 107 (1985) 723.
- 15 D. Wirth and D. M. Lemal, *J. Am. Chem. Soc.*, 104 (1982) 847.
- 16 I. G. Pitt, R. A. Russell and R. N. Warrener, *J. Am. Chem. Soc.*, 107 (1985) 7176.
- 17 Z. Latajka, H. Ratajczak, W. J. Orville-Thomas and E. Ratajczak, *J. Mol. Struct.*, 85 (1981) 303.
- 18 D. Price and E. Ratajczak, *Int. J. Mass Spectrom. Ion Phys.*, 60 (1984) 203.
- 19 E. Ratajczak, *Rocz. Chem.*, 44 (1970) 447.
- 20 J. Collin, *Bull. Soc. Chem. Belg.*, 19 (1960) 449.
- 21 E. Stenhagen, S. Abrahamsson and F. McLafferty, *Registry of Mass Spectral Data*, Wiley, 1974.
- 22 E. E. van Tamelen and T. H. Whitesides, *J. Am. Chem. Soc.*, 93 (1971) 6129.
- 23 E. E. van Tamelen and S. B. Pappas, *J. Am. Chem. Soc.*, 85 (1963) 3297.

- 24 I. Haller, *J. Phys. Chem.*, 72 (1968) 2882.
- 25 E. Ratajczak and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, (1968) 509.
- 26 E. Ratajczak, *Bull. Chem. Polon. Sci., Ser. Sci. Chim.*, 21 (1973) 691.
- 27 B. Sztuba and E. Ratajczak, *J. Chem. Soc., Perkin Trans. II*, (1982) 823.
- 28 J. T. Jodkowski and E. Ratajczak, *Bull. Pol. Acad. Sci., Chem.*, 31 (1983) 167.
- 29 M. G. Barlow, J. G. Dingwall and R. N. Haszeldine, *J. Chem. Soc., Chem. Commun.*, (1970) 1580.
- 30 Y. Kobayashi, I. Kumadaki, A. Ohsawa and Y. Sekine, *Tetrahedron Lett.*, (1975) 1639.