

FLASH PHOTOLYSIS STUDY OF 1-PHENYLPYRROLE

O. SANTOS and A. C. TESTA

Department of Chemistry, St. John's University, Jamaica, NY 11439 (U.S.A.)

M. O'SULLIVAN

Department of Chemistry, Richmond College, Staten Island, NY 10301 (U.S.A.)

(Received May 16, 1983; in revised form June 22, 1983)

Summary

A flash photolysis study of 1-phenylpyrrole indicates that a major primary event is fission of the phenyl-pyrrolyl bond, leading to radicals which recombine as well as react. A variable-temperature study in isopropyl alcohol indicates that this process still occurs at -95°C ; however, a second photochemical event requiring diffusion and thermal activation is removed upon cooling. The observation of a 360 nm transient with a half-life of 0.5 ms in four different solvents is attributed to the triplet-triplet absorption of biphenyl. The formation of 2-phenylpyrrole absorbing at 290 nm provides further evidence for the primary event leading to phenyl radicals.

1. Introduction

The photoexcitation of aromatic molecules often leads to photodissociation and photoionization. In cases when these two primary events dominate, identification of the species by the flash photolysis method has been very useful [1]. In continuing the interest of this laboratory in the excited state behavior of aromatic nitrogen heterocyclics we have undertaken an investigation of the flash photolysis behavior of 1-phenylpyrrole.

Pyrrole derivatives in solution are known to undergo photoisomerization, photosubstitution, photocyclization and photoreduction [2-5]. Photoisomerization of 1-benzylpyrrole leads to the formation of the 2-substituted and 3-substituted isomers, with a predominance of the former [6]. The cation of 1-phenylpyrrole has been generated by photolyzing the corresponding arenediazonium salt [7].

1-phenylpyrrole has the interesting potential of generating phenyl and pyrrolyl radicals, which can lead to the following recombination products:





In fact the production of biphenyl, bipyrrrole and phenyl pyrroles as well as reactions of the primary radicals with the solvent are all viable possibilities. There are only four distinct ways in which photoproducts can be produced when the phenyl and pyrrolyl radicals recombine: (i) biphenyl; (ii) bipyrrrole; (iii) 2-phenylpyrrole; (iv) 3-phenylpyrrole. In probing this system we decided to use temperature variation as a means of controlling the competition between unimolecular and bimolecular events. With the aim of determining the involvement of some of these processes in the photolysis of 1-phenylpyrrole, we have taken two different approaches: (a) a flash photolysis investigation of 1-phenylpyrrole in various solvents including temperature variation and (b) a phosphorescence and photoexcitation study at 77 K.

2. Experimental details

2.1. Materials

1-phenylpyrrole obtained from the Aldrich Chemical Co. was purified by dissolving in ethanol and reprecipitating by the addition of water, followed by vacuum sublimation. Spectrograde solvents (cyclohexane, diethyl ether, isooctane, isopropyl alcohol, acetonitrile and ether-isopentane-ethanol (EPA)) were obtained from Matheson, Coleman & Bell and were used as received. The concentration of 1-phenylpyrrole was typically 2×10^{-4} M.

2.2. Apparatus

The flash photolysis apparatus used in these studies has been described elsewhere [8]. Room temperature measurements were performed in a cell of path length 12 cm, while variable-temperature measurements were made using a cell of path length 10 cm mounted in a clear Suprasil Dewar. Photoexcitation at 77 K was performed using a high pressure mercury lamp after mounting the sample in a Suprasil cell of path length 3 mm held in a quartz Dewar filled with liquid nitrogen. In most cases an unfiltered HBO 100 W/2 mercury lamp was used for excitation. Qualitative UV spectra at 77 K were recorded using a Cary model 14 spectrophotometer and the same optical

Dewar that was used for excitation and were measured relative to air or in some cases a neutral density screen.

3. Results

The flash photolysis at room temperature of vacuum degassed 1-phenylpyrrole in isopropyl alcohol, acetonitrile, isooctane and diethyl ether led to an absorbing transient with a wavelength maximum of 360 nm and a lifetime of 0.5 ms. No transient was observed in air-saturated solutions. A second transient with a lifetime of 0.6 ms appeared at 520 nm in isopropyl alcohol. Figure 1 shows the absorption spectrum of the transient observed at room temperature. Repeated flashing led to photochemical disappearance as evidenced by the decreasing absorption in the 253 nm region and the growth of a new band at 290 nm, as is seen in Fig. 2.

Since the 360 nm transient was most intense for isopropyl alcohol solutions variable-temperature studies were performed in this solvent. Upon cooling, some intensification of the 360 nm transient and lengthening of the lifetime was observed; however, almost complete disappearance of the 520 nm band occurred. The 360 nm transient lifetime increased from 1.5 to 15 ms in the temperature range from -10 to -95 °C, and its spectrum recorded at -95 °C is shown in Fig. 1, curve 5. The temperature dependence of the lifetime of the 360 nm band is summarized in Fig. 3.

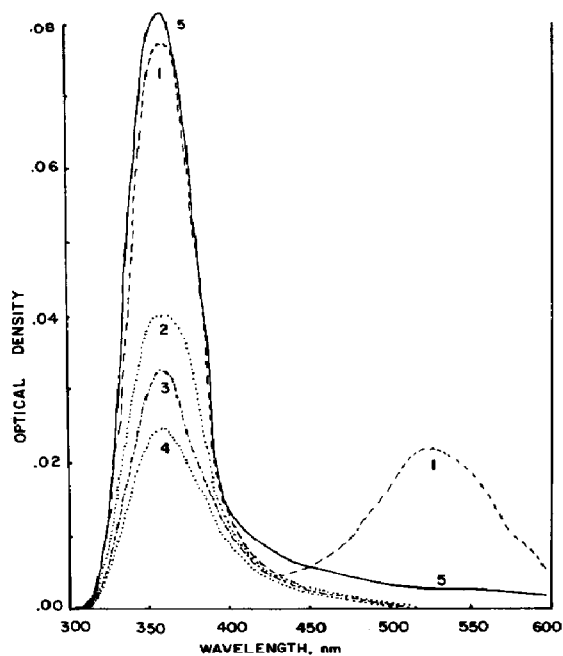


Fig. 1. Transient absorption spectra observed for the flash photolysis of a vacuum degassed solution of 2×10^{-4} M 1-phenylpyrrole in various solvents: curve 1, at 25 °C in isopropyl alcohol; curve 2, at 25 °C in acetonitrile; curve 3, at 25 °C in ethyl ether; curve 4, at 25 °C in isooctane; curve 5, at -95 °C in isopropyl alcohol.

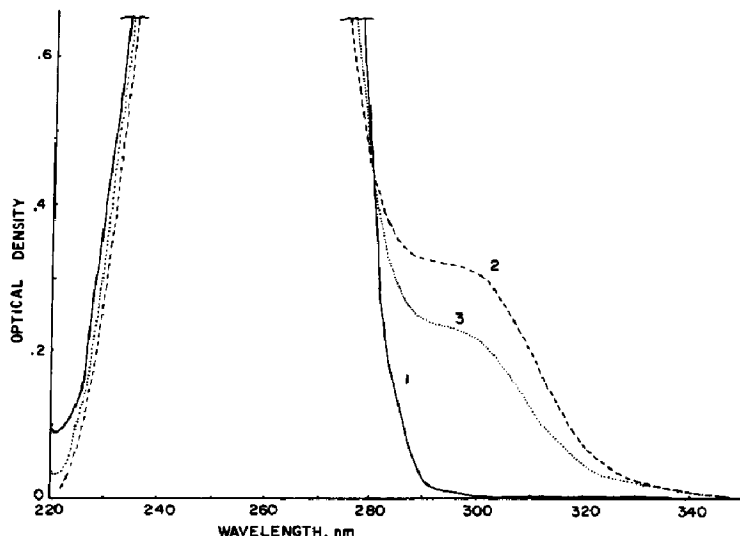


Fig. 2. UV absorption spectra of a vacuum degassed solution of 2.4×10^{-4} M 1-phenylpyrrole in isopropyl alcohol (all measured at 298 K): curve 1, prior to flashing; curve 2, after flashing at room temperature; curve 3, after flashing at -95°C and thawing to room temperature.

The phosphorescence spectrum of 1-phenylpyrrole in isopropyl alcohol at 77 K is shown in Fig. 4, curve 1, and its phosphorescence lifetime was determined to be 1.4 s. Irradiation with the full intensity of a high pressure mercury lamp at 77 K led to a decreasing phosphorescence intensity with time as is shown in Fig. 4, curve 2. Upon thawing and refreezing, however, the phosphorescence signal increased and is shown in Fig. 4, curve 3. Renewed illumination at 77 K decreased the phosphorescence intensity again, and thawing to room temperature followed by refreezing led to increased phosphorescence due to the generation of photoproducts.

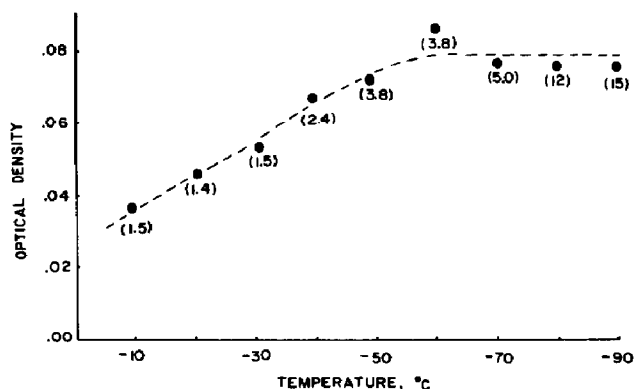


Fig. 3. Variation in the 360 nm transient lifetime and optical density with temperature in the range from -10 to -90°C for a vacuum degassed solution of 2.4×10^{-4} M 1-phenylpyrrole in isopropyl alcohol. The values given in parentheses are the lifetimes in milliseconds.

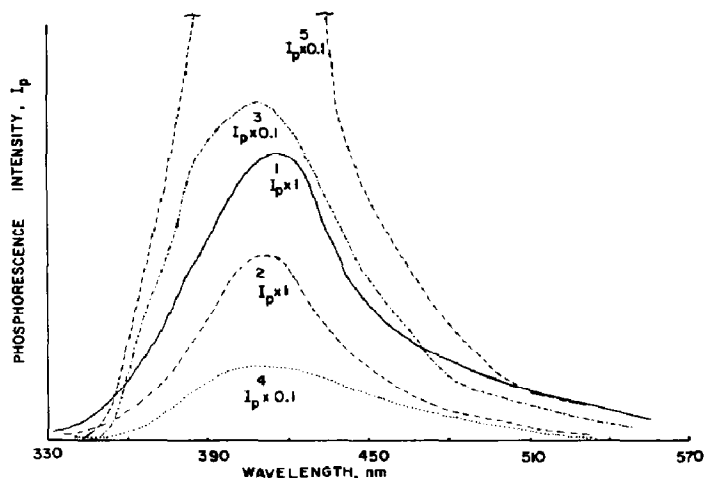
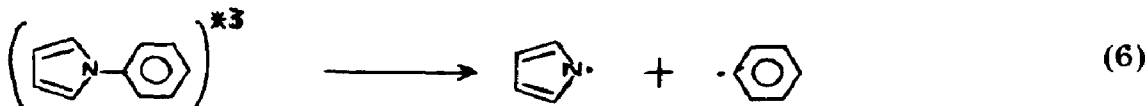


Fig. 4. Phosphorescence behavior at 77 K of an air-saturated solution of 2×10^{-4} M 1-phenylpyrrole in isopropyl alcohol (excitation with unfiltered high pressure mercury lamp): curve 1, $t = 0$; curve 2, after 10 min irradiation at 77 K; curve 3, after thawing and recooling sample 2; curve 4, after 10 min irradiation of sample 3; curve 5, after thawing and recooling sample 4.

4. Discussion

The transient observed at 360 nm with a lifetime of 0.5 ms is probably due to a unimolecular event since it is observed in a variety of solvents. Moreover, it cannot be the triplet since a photodissociative mode is occurring based on the UV absorption spectrum of 1-phenylpyrrole before and after flashing. The absence of a transient in air-saturated solutions is consistent with a bond fission via the triplet state. From a comparison of the 360 nm transient spectrum and lifetime with that for biphenyl [1, 9 - 11], we conclude that it is due to the triplet-triplet (T-T) absorption of biphenyl, thus providing clear evidence that one of the primary photochemical processes in 1-phenylpyrrole is fission of the C-N bond between phenyl and pyrrolyl:



Further support for the formation of biphenyl is that it is observed in four different solvents.

In addition to the observed disappearance of 1-phenylpyrrole in the flash experiment the growth of a photoproduct at 290 nm after flashing can readily be assigned to 2-phenylpyrrole, whose wavelength absorption maximum is known [12]. The photoisomerization of pyrrole derivatives

from the 1-substituted to the 2-substituted isomer has been reported [6]. The propensity of 1-phenylpyrrole to undergo sensitized photosubstitution, preferentially at the 2 position, has been shown by Yoshida [13]. The phenyl migration from the 1 to the 2 position that we observed at room temperature, and to a lesser extent at -95°C in isopropyl alcohol, is consistent with the primary C—N fission's requiring very little activation.

As expected, the data from the variable-temperature flash photolysis study of the 360 nm band (T—T absorption of biphenyl) in isopropyl alcohol indicate that the biphenyl triplet lifetime is lengthened by cooling. The phosphorescence lifetime of biphenyl in EPA at 77 K is 4.1 s [14]. More important, however, is the disappearance of the 520 nm band upon cooling, which indicates that it originates in a bimolecular event requiring interaction with the solvent. The continuing participation of the phenyl radicals even at -95°C , as evidenced by the biphenyl T—T absorption, reflects the facile recombination of these radicals. In fact the slight increase in optical density at 360 nm observed at low temperatures, coupled with the disappearance of the weaker band at 520 nm upon cooling, indicate that the latter, which has a larger activation energy than that of radical recombination, probably involves reaction with the solvent, *i.e.* hydrogen abstraction or solvent addition.

Although we have been unable to obtain evidence for photoionization in this system, it is reasonable to conclude from the decreasing phosphorescence with irradiation at 77 K that the primary event originating in the triplet state is fission of the C—N bond between the two rings with some of the recombination events leading to (1) biphenyl and (2) 2-phenylpyrrole. The biphotonic photoionization of biphenyl in rigid hydrocarbon glasses at 77 K has been shown to proceed through the triplet [15]. In view of the possibility that the recombination of two phenyl radicals to generate biphenyl can lead to singlet and triplet biphenyl, we also flashed photolyzed biphenyl in isopropyl alcohol in the concentration range 2×10^{-4} - 2×10^{-5} M at the same energy input that we used for 1-phenylpyrrole. These experiments indicated very little transient at 360 nm compared with the signals observed when flashing 1-phenylpyrrole directly. We conclude from this behavior that biphenyl triplets are partially formed upon recombination of two phenyl radicals; however, we are unable to rule out energy transfer to the lowest triplet of biphenyl ($23\,000\text{ cm}^{-1}$ [10, 16]) from the lowest triplet of 1-phenylpyrrole as the origin of biphenyl triplets.

References

- 1 H. I. Joschek and L. I. Grossweiner, *J. Am. Chem. Soc.*, **88** (1966) 3261.
- 2 H. Shizuka, S. Ono, T. Morita and I. Tanaka, *Mol. Photochem.*, **3** (1971) 203.
- 3 M. Bellas, D. B. Smith and A. Gilbert, *Chem. Commun.*, **6** (1967) 263.
- 4 T. Kubata and H. Sakurai, *Chem. Lett.*, **10** (1972) 923.
- 5 O. Buchardt (ed.), *Photochemistry of Heterocyclic Compounds*, Wiley, New York, 1976, pp. 127 - 129.

- 6 J. M. Patterson and L. T. Burka, *Tetrahedron Lett.*, (1969) 2215.
- 7 H. B. Ambroz and T. J. Kemp, *J. Chem. Soc., Perkin Trans. II*, (1980) 768.
- 8 J. Wolleben and A. C. Testa, *J. Photochem.*, 8 (1978) 125.
- 9 G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A*, 245 (1958) 238.
- 10 I. A. Ramsay and I. H. Munro, in A. B. Zahlan (ed.), *The Triplet State*, Cambridge University Press, Cambridge, Cambs., 1967, p. 415.
- 11 W. Heinzelmann and H. Labhart, *Chem. Phys. Lett.*, 4 (1969) 20.
- 12 B. Elpern and F. C. Nachod, *J. Am. Chem. Soc.*, 72 (1950) 3377.
- 13 K. Yoshida, *J. Chem. Soc., Chem. Commun.*, (1978) 1108.
- 14 M. Zander, *Z. Naturforsch.*, 32a (1977) 339.
- 15 W. A. Gibbons, G. Porter and M. I. Salvadatti, *Nature (London)*, 206 (1965) 1356.
- 16 S. P. McGlynn, T. Azumi and M. Kinoshita, *Molecular Spectroscopy of the Triplet State*, Prentice-Hall, Englewood Cliffs, NJ, 1969, p. 383.