around the C_1–C_2 bond by the large displacement vector of H_a. Also we see that the chemical bond of C_1–C_2 changes from a double to a single bond. As a result, the bond length increases along the reaction coordinate from 1.316 Å (EVE) to 1.389 Å (TS(1a)) and 1.508 Å (CH_3CHO). The corresponding vibrational frequency of the stretching mode varies from 1637 to 1545 and 1088 cm^{-1}, respectively. This mode corresponds to the reaction coordinate of the decomposition of acetaldehyde. Thus it is probable that the stretching of the C_1–C_2 bond of the activated molecule through TS(1a) gains an excess energy of 457 cm^{-1}. Although this excess energy is small compared with the thermal energy, if this energy remains effectively localized in this mode, the rate of the second step becomes larger than the rate in the thermally equilibrated system. Thus, in the chemical activation of the fragment produced from the thermal decomposition there are three characteristics: (1) the fragment has a energy higher than the potential barrier of the first step, (2) it has a special geometry and motions of each nucleus determined by the structure of the TS of the first step, and (3) the excess energy is localized in a particular vibrational mode depending on the mode coupling in the produced fragment. We may expect, from the above features, the observed difference in the second-step reaction rate and the special selection of the competing reaction paths between the *normal* molecules and the *fragment* molecules produced from the thermal decomposition.

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Matrix-Controlled Photochemistry of Benzene and Pyridine

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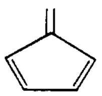
Dewar benzene has been shown to be a primary product from the photolysis of benzene in low temperature argon matrices at 253.7 nm. This is the first observation of Dewar benzene production at this wavelength and a mechanism is proposed that involves benzene S_1–S_2 state mixing induced by the matrix environment. Analogous experiments on the photolysis of pyridine show that the only primary products are isomeric species derived at least in part from a triplet state of pyridine, probably T_1. This is the first observation of photochemistry from the T_1 state and may be the process responsible for the small values of τ_p and ϕ_p in pyridine. Analysis of the IR spectral bands points to the main product being Dewar pyridine although other isomers cannot be ruled out. In contrast to the gas phase, no decomposition of pyridine was found in matrices producing compounds such as acrylonitrile, ethyne, and hydrogen cyanide.

Introduction

Aromatic molecules can undergo remarkable photochemical transformations. Benzene has been the most widely studied compound partly because many research workers have postulated the intermediacy of a "physical isomer" in the so-called "channel 3" decay process.[1] A similar phenomenon is also observed at the onset of the $S_0 \rightarrow S_2$ transition in pyridine.[2] It has been observed that isomer production from the direct photolysis of benzene is wavelength and phase dependent. Benzvalene (**1**) and fulvene (**2**) are produced in the liquid-phase photolysis at 253.7 nm[3] and Dewar benzene (**3**) is observed after 204-nm photolysis in condensed phases.[4] In the vapor phase benzvalene production is seen to be wavelength and temperature dependent within the $S_0 \rightarrow S_1$ band system, indicating a need for activation before isomerization proceeds. The photolysis of gaseous benzvalene at 253.7 nm produces both benzene and fulvene, although the latter compound may result from a thermal wall-induced reaction.[5,6]

It has been shown by NMR spectroscopy that excitation of pyridine in aqueous sodium borohydride with a low pressure mercury lamp gives Dewar pyridine (**4**) as an intermediate product with a half-life at 25 °C of $2^1/_2$ min.[7] No reports of the aza analogues of fulvene or benzvalene have been reported, although the flash photolysis of pentafluoropyridine produces two isomers of azafulvene with lifetimes of several milliseconds.[8]


(1)


(2)


(3)


(4)

Benzene has been the subject of several matrix spectroscopic and photophysical studies, although no photochemical reactions of benzene have hitherto been reported in low temperature solids.[9-12] Pyridine has been less well studied under these conditions, though Chapman et al. reported that HCN and cyclobutadiene were the products of pyridine photolysis at 8 K in an argon matrix.[13] They suggest the reaction proceeds through a valence tautomer such as Dewar pyridine, although no evidence was presented to support this. Photofragmentation has also been observed in the gas phase.[14]

In this study, benzene and pyridine have been photolyzed at low temperatures so that photolysis products that are unstable at room temperature can be identified. In addition, the effects of enhanced photophysical processes such as intersystem crossing (by employing a heavy atom matrix gas) and vibrational relaxation

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(1) Phillips, D.; Lemaire, J.; Burton, C. S.; Noyes, W. A.; *Adv. Photochem.* **1968**, *5*, 329.
(2) Yamazaki, I.; Baba, H. *Discuss. Faraday Soc.* **1983**, *75*, 395.
(3) Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1031.
(4) Ward, H. R.; Wishnok, J. S. *J. Am. Chem. Soc.* **1968**, *90*, 1086.
(5) Kaplan, L.; Wilzbach, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 3291.
(6) Kent, J. E.; Harman, P. J.; O'Dwyer, M. F.; Griffith, D. W. T. *J. Phys. Chem.* **1981**, *85*, 2731.
(7) Wilzbach, K. E.; Rausch, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 2178.
(8) Ratajczak, E.; Stuba, B.; Price, D. *J. Photochem.* **1980**, *13*, 233.
(9) Robinson, G. W. *J. Chem. Phys.* **1967**, *47*, 1967.
(10) Robinson, G. W. *J. Chem. Phys.* **1960**, 934.
(11) Katz, B.; Prith, M.; Sharf, B.; Jortner, J. *J. Chem. Phys.* **1971**, *54*, 3924.
(12) Sodeau, J. R. Ph.D. Thesis, University of Southampton, 1976.
(13) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614.
(14) Mathias, E.; Heicklen, J. *Mol. Photochem.* **1972**, *4*, 483.

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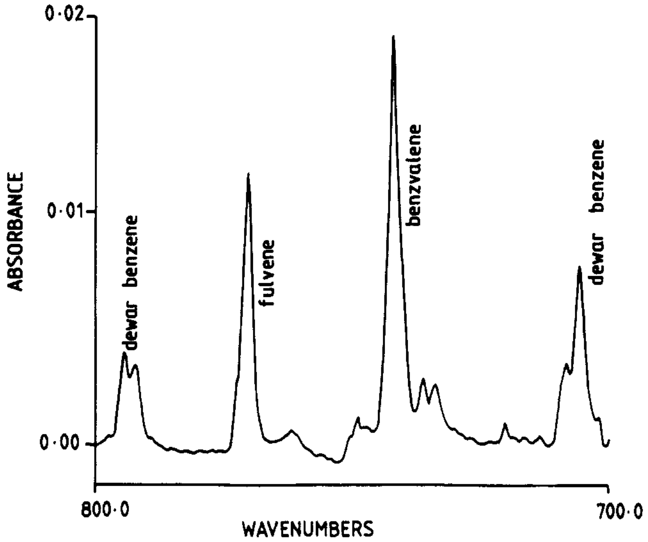

Figure 1. FTIR spectrum of benzene in argon, MR = 1:1000, after 6-h photolysis at 253.7 nm (700–800 cm^{-1} region).

(due to the cold matrix cage) on any observed photochemistry has been explored.

Experimental Section

A Heliplex CS-308 closed cycle helium refrigeration system (Air Products Inc.) was used to maintain a cesium iodide deposition window at the normal operating temperature of 4.2 K as measured by an Air Products APD-H controller and a helium vapor bulb pressure gauge. Infrared radiation from an external Perkin-Elmer globar source was passed through a cesium iodide window, the outer potassium bromide windows of the vacuum shroud, and the emission port of a Digilab FTS 80V Fourier transform infrared spectrometer fitted with a Mercury Cadmium Telluride detector cooled to liquid nitrogen temperature. All spectra were collected as single beams at 1 cm^{-1} resolution and computed from the coaddition of 1024 interferograms. These were then ratioed against a suitable background to produce the required absorbance spectrum; this enables an "after photolysis" single beam spectrum to be ratioed against a "before photolysis" spectrum so that the resultant absorbance spectrum shows "new" products to be pointing upward and reactants downward.

Phosphorescence lifetimes were recorded on a Farrand Mk II spectrofluorimeter by chopping the excitation source and monitoring the phosphorescence decay as a function of time on a chart recorder. The data were analyzed by using ENZFITTER (Elsevier Biosoft, 1987).

Matrices were deposited on the cold window via the pulsed deposition technique and photolysis light was transmitted through a Spectrosil-B window present in the vacuum shroud. All photolyses were achieved with a low pressure mercury discharge lamp (Phillips 93109E) fitted with a 2-mm thick vycor glass filter to remove any incident 184.9-nm radiation.

Matrix mixtures were made up on a standard mercury-free vacuum line fitted with greaseless taps and matrix ratios were calculated from pressure measurements obtained from two MKS baratron units (Models 220B, 222HSA).

Argon and xenon of stated purity 99.999% were purchased from Messer Greisheim (Distillers) and passed through a glass spiral immersed in an appropriate coolant so as to remove any residual water vapor or carbon dioxide. Benzene and pyridine (99%) were purchased from Aldrich and were distilled and degassed repeatedly before use.

Results

Benzene. Benzene in argon (matrix ratio = 1:1000) was photolyzed at 253.7 nm for 6 h after which several new bands appeared in the IR spectrum. The spectral region 800–700 cm^{-1} is shown in Figure 2 and all new product bands are listed with their assignments in Table I. Identification of the products was made by comparison to the previously recorded matrix isolated spectra of the benzene photoisomers.[15,16] It is clear that benzvalene, fulvene, and Dewar benzene are all produced. This contrasts with gas- and liquid-phase results where only fulvene and benzvalene are observed after 253.7-nm photolysis. The experiment was repeated in a xenon matrix, in order to investigate any "heavy atom effect" on the observed photochemistry, but in this case no photolysis products were observed.

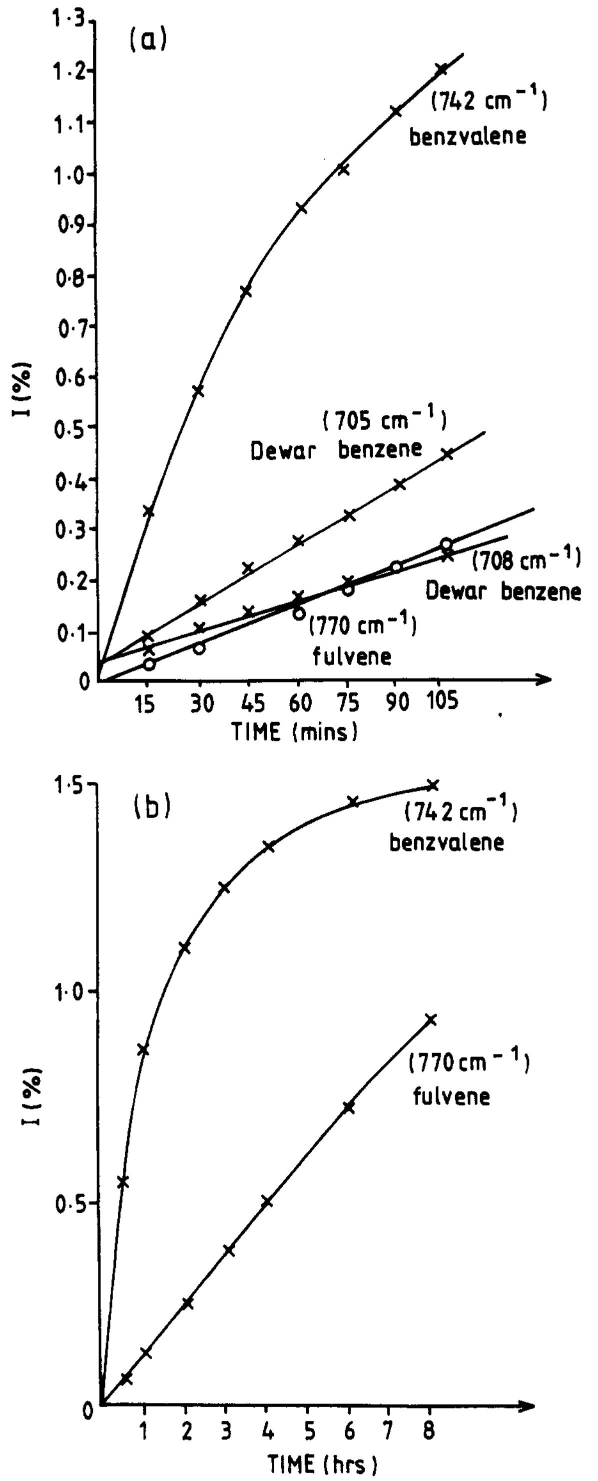

Figure 2. Serial photolysis experiment of benzene in argon (a) 0–105 min time scale; (b) 0–8 h time scale.

A serial photolysis experiment in which the infrared absorbance peak height is recorded as a function of photolysis duration can

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(15) Griffith, D. W. T.; Kent, J. E.; O'Dwyer, M. F. *Aust. J. Chem.* **1975**, *28*, 1397.

(16) Domaille, P. J.; Kent, J. E.; O'Dwyer, M. F. *Aust. J. Chem.* **1974**, *27*, 2463.

TABLE I: New Bands in FTIR Spectrum of Benzene in Argon (MR = 1:1000) Photolyzed at 253.7 nm

band, cm^{-1}	assignment	band, cm^{-1}	assignment
616.3	fulvene	937.0	Dewar benzene
705.9	Dewar benzene	948.8	fulvene
708.4	Dewar benzene	1078.7	Dewar benzene/fulvene
742.6	benzvalene	1081.1	Dewar benzene/fulvene
770.6	fulvene	1089.8	benzvalene
792.7	Dewar benzene	1135.6	Dewar benzene
794.7	Dewar benzene	1148.6	Dewar benzene
811.5	benzvalene	1166.0	benzvalene
823.1	Dewar benzene	1270.1	Dewar benzene
826.0	Dewar benzene	1272.1	Dewar benzene
848.2	benzvalene	1312.6	benzvalene
894.5	fulvene	1313.5	benzvalene
926.3	fulvene	1342.8	fulvene

distinguish primary and end products and those that are intermediates that can go on to "react" further. Shown in Figures 2a and 2b are two such plots for the prominent bands of Dewar benzene, fulvene, and benzvalene, after benzene in argon (MR = 1/1000) was photolyzed at 253.7 nm. Note that the profiles for fulvene and Dewar benzene are linear, whereas that for benzvalene tends toward a steady value. It is also evident that the two bands comprising the doublet at 705 and 708 cm^{-1} have different slopes, indicating different rates of Dewar benzene production. However, this is not unexpected since initially, benzene molecules are distributed between several geometrically distinct sites (with differing matrix concentrations) and that, as will be discussed below, the site geometry has a pronounced effect on the observed photochemistry.

From Figures 2a and 2b, it appears that benzvalene exhibits the temporal behavior usually associated with that of an intermediate species whereas fulvene and Dewar benzene appear to be either primary products that do not react further or secondary products derived from an appropriate intermediate.

The phosphorescence lifetime of benzene in argon at 4.2 K was obtained by shutting off the excitation source of the fluorimeter and monitoring the subsequent emission (λ_{max} = 356 nm) as a function of time. The experimental data could be fitted to a double exponential decay of the form

$$I(t) = A_1e^{-k_1t} + A_2e^{-k_2t}$$

where A_1 and A_2 are simple weighting factors, k_1 and k_2 are the rate coefficients associated with the decay process, and the lifetime components of phosphorescence emission are given by

$$\tau_1 = \frac{1}{k_1};\quad \tau_2 = \frac{1}{k_2}$$

The curve fit gave lifetime components of $\tau_1 \approx 19.1$ s; and $\tau_2 \approx 10.1$ s.

The fact that the emission characteristics are reproduced better by a double-exponential decay rather than a single-exponential function is not surprising since benzene is known to have several site-dependent lifetimes of phosphorescence in low temperature matrices.[17] Thus the data indicate the presence of more than one site geometry when benzene is matrix isolated at 4.2 K. The implication of this observation will be discussed more fully below.

Pyridine. Pyridine in an argon matrix (MR ratio = 1:1000) was photolyzed at 253.7 nm for 3 h. The resulting product bands are listed in Table II and the spectral region 825–1025 cm^{-1} is shown in Figure 3.

TABLE II: New Bands in FTIR Spectra of Pyridine in Argon (MR = 1:1000) Photolyzed at 253.7 nm (after Photolysis)

band	(rel intensity)	band	(rel intensity)
706.4	(0.48)	976.9	(0.09)
730.1	(1.05)	1001.1	(0.16)
732.5	(0.88)	1034.8	(0.38)
734.9	(0.72)	1047.3	(0.23)
802.4	(0.45)	1067.6	(0.10)
819.3	(0.38)	1129.6	(0.53)
823.1	(0.85)	1139.0	(0.08)
827.9	(0.48)	1172.2	(0.08)
852.9	(0.31)	1175.6	(0.08)
859.8	(0.10)	1178.0	(0.08)
874.2	(0.61)	1255.7	(0.62)
895.0	(0.26)	1275.7	(1.96)
946.1	(0.25)	1278.3	(0.29)
960.5	(0.16)	1442.8	(0.7)
962.0	(0.18)		

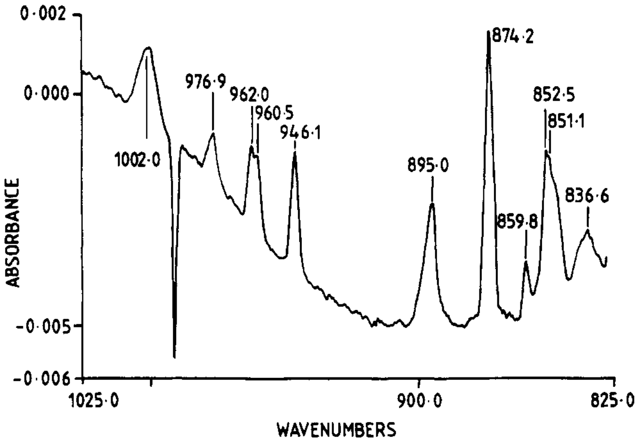

Figure 3. FTIR spectrum of pyridine in argon MR = 1:1000, after 3-h photolysis at 253.7 nm (825–1025 cm^{-1} region).

In contrast to benzene, the possibility exists that the observed products result from fragmentation of the pyridine ring. By analogy with other studies, expected products would appear to be ethyne and acrylonitrile or hydrogen cyanide and cyclobutadiene. In the present work each of the above stable molecules was isolated in argon and its infrared spectrum recorded. For the other case, namely, cyclobutadiene, comparison was made with previously reported spectra in matrices.[13] The former procedure is preferable since two distinct products will be formed as partners within the same matrix cage and might therefore be expected to undergo a degree of complexation so shifting their "isolated" infrared frequencies. Thus matrices containing ethyne and acryonitrile in argon (MR = 1:1:1000) and also ethyne/HCN in argon (MR = 1:1:1000) were deposited and annealed before recording their infrared spectra. No bands from these latter experiments or from literature reports of the unstable species were found to be coincident with those from the matrix photolysis of pyridine alone. For example, no band corresponding to the intense ν_3 mode of ethyne in argon matrices at 3289 cm^{-1} was observed in any of our photolysis experiments although it was apparent in the ethyne/HCN/Ar mimic. Hence it can be concluded that, in contrast to the work of Chapman and related gas-phase experiments by other workers, isomers alone are produced in the present experiments rather than fragmentation products.

As with benzene the peak height absorbance of several of the isomer product bands from the pyridine photolysis was plotted as a function of photolysis time. All the plots were linear, indicating, in contrast to benzene, that no intermediates are involved and that the product(s) must be primary in nature.

Again by analogy with the benzene experiments, pyridine in xenon (MR = 1:1000) was photolyzed at 253.7 nm for 3 h. The intensities of the pyridine bands before photolysis and those after photolysis in both argon and xenon matrices are shown in Table III. Changing the matrix gas from argon to xenon often results in small IR spectral shifts (due to differing solvent cage PE functions). It can also lead to the formation of differing site environments and modifications to the infrared spectral intensities. In this study, it can be seen that there are some small fluctuations in the intensities of corresponding pyridine bands in the two matrices before photolysis, but a clear product enhancement is observed in the xenon matrix for both identical photolysis periods and initial matrix concentrations of parent. These results show, in contrast to benzene, that a "heavy atom" effect is important

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(17) Johnson, P. M.; Ziegler, L. *J. Chem. Phys.* **1972**, *56*, 2169.
(18) Korppi-Tommola, J. *J. Mol. Struct.* **1977**, *40*, 13.

TABLE III: FTIR Band Intensities for Pyridine and Argon and Xenon Matrices (before and after 253.7-nm Photolysis)

before photolysis		after photolysis	
argon	xenon	argon	xenon
602.1 (3.3)	601.2 (1.9)	730.1 (1.05)	725.9 (2.5)
701.4 (31.3)	698.6 (19.1)	732.5 (0.88)	728.1 (1.2)
705.6 (2.2)	705.9 (5.3)	734.9 (0.72)	730.8 (1.4)
	741.4 (6.1)	802.4 (0.45)	799.6 (0.6)
744.4 (6.0)	745.9 (1.8)	819.3 (0.38)	
991.8 (4.0)	989.2 (3.3)	823.1 (0.85)	821.4 (1.7)
1032.2 (6.8)	1029.8 (7.0)	827.9 (0.45)	
1144.8 (0.5)			845.9 (0.6)
1146.2 (0.8)	1144.2 (3.0)	851.5 (0.31)	848.2 (0.6)
1147.7 (1.52)		874.2 (0.6)	869.1 (0.8)
	1437.8 (14.2)	895.0 (0.26)	892.7 (0.43)
1440.9 (25.2)	1442.4 (6.9)		943.5 (0.5)
1483.6 (4.5)	1480.4 (4.8)	946.1 (0.25)	944.9 (0.5)
	1574.8 (1.4)	960.5 (0.16)	958.5 (0.4)
1579.5 (4.7)	1579.9 (6.5)	962.0 (0.18)	960.1 (0.5)
1583.4 (10.7)	1581.4 (3.8)	1047.3 (0.23)	1044.4 (0.65)
1592.2 (1.8)	1595.1 (4.8)	1129.6 (0.53)	1126.1 (1.4)
1599.3 (5.4)		1139.0 (0.08)	1135.1 (0.4)
		1172.2 (0.08)	1171.5 (0.2)
		1175.6 (0.08)	1174.5 (0.3)
		1178.0 (0.08)	
		1255.7 (0.62)	1252.0 (0.9)
			1253.6 (0.4)
		1275.4 (1.96)	1271.7 (3.4)

with pyridine matrix photochemistry.

Discussion

Photoisomerization Mechanisms of Benzene in Matrices. The photolysis of benzene in low temperature matrices at 253.7 nm has shown that both benzvalene and fulvene are products and more importantly so is Dewar benzene. This is the first observation of the formation of Dewar benzene at this wavelength and is in conflict with liquid- and vapor-phase results where only fulvene and benzvalene have hitherto been reported. At this stage it should be noted that the product of Dewar benzene is normally associated with the higher singlet states S_2 ($^1B_{1u}$) and S_3 ($^1E_{1u}$) of benzene. This assertion has been shown experimentally by using compounds able to efficiently "trap" triplet states.[19]

However one further potential source of Dewar benzene to be considered in a matrix is the T_1 triplet state. Excitation at 253.7-nm populates the S_1 ($^1B_{2u}$) state of benzene, which in the gas phase undergoes intersystem crossing with a triplet quantum yield of 0.71 at room temperature.[20] T_1 ($^3B_{1u}$) has the same symmetry in D_{6h} as S_2 ($^1B_{1u}$) and since Dewar benzene is associated with this electronic state, then T_1 may be responsible for the observed Dewar benzene. The quantum yield of triplet formation in a xenon matrix has been previously measured as unity[21] (due to "external heavy atom effect") but since no photolysis products were detected in the present xenon experiments T_1 cannot be involved in the isomerization process.

A more subtle mechanism for Dewar benzene formation can be proposed that allows for S_1–S_2 state mixing and thereby explains the experimental observations. The S_0 ($^1A_{1g}$) → S_1 ($^1B_{2u}$) transition in gas-phase benzene molecules is dipole forbidden but gains an in plane transition moment through pseudo-Jahn–Teller vibronic coupling of the S_1 state to the $^1E_{1u}$ (S_3) state via an e_{2g} mode (such that $B_{2u} \times E_{2g} = E_{1u}$). Coupling between S_1 and S_2 ($^1B_{2u}$) is via and a_{2g} mode. However in an argon crystal it has been shown that a benzene molecule occupies sites of well-defined symmetry (e.g., D_{3h}, D_{2h}, C_{2h}, C_{2v}) as shown by site-resolved phosphorescence lifetimes.[17] The lifetime experiments performed in this work gave τ values of 10.1 and 19.1 s; a high resolution study by Johnson et al. revealed several lifetimes, the two most prominent values being 11.7 and 17.5 s. So if it is assumed that the benzene molecule is slightly distorted such that it assumes the symmetry of the site it occupies, then coupling may occur via the e_{2g} mode involved in the initial excitation. Table IV contains symmetry correlations appropriate for changes from D_{6h} to each of the various site symmetries in an argon crystal. It also lists the direct products $B_{2u} \times e_{2g}$ (in D_{6h}) for each of the point groups D_{3h}, D_{2h}, C_{2h} and C_{2v}.

In all of the 2-fold sites the direct product has the same symmetry as the S_2 state of benzene. Thus initial excitation at 253.7 nm will allow state mixing of S_1 and S_2 in the sites and hence a route to Dewar benzene exists in the matrix environment. Evidence that $S_1 \rightarrow S_2$ mixing is indeed responsible for the production of Dewar benzene can be inferred from the analogous photolysis of hexafluorobenzene (HFB).

Irradiation of hexafluorobenzene in the liquid or vapor phase produces only hexafluoro(Dewar benzene) and is apparently an excited state singlet process.[22] Phillips concluded that excitation at $\lambda < 280$ nm gave rise to two excited singlet states, one of which decays rapidly to the fluorescent state whereas the other appears to undergo efficient isomerization.[23] Bryce-Smith suggested that the precursor might be a vibrationally excited S_2 state[24] and in fact a similar photolysis experiment by Suijker et al. resulted in a transient, which could not be identified with either S_1 or T_1.[25] These results are not surprising when the UV spectrum of HFB is analyzed.[24] It shows the S_1 and S_2 states to be close in energy and overlap to a greater extent than in the case of benzene. It is therefore reasonable to postulate that the hexafluoro(Dewar benzene) originates from intrinsic S_2–S_1 state mixing whereas the photoproduction of Dewar benzene in a matrix results from "site-perturbed" S_2–S_1 state mixing.

From the serial photolysis experiments summarized in Figure 2, it is clear that fulvene exhibits a linear dependence of concentration with time, whereas the benzvalene profile indicates a steady state behavior. These contrasting results can be explained in terms of the differing photochemistry of the two isomers. Although the molar absorption coefficients of benzvalene and benzene are 10 and 200 L mol^{-1} cm^{-1}, respectively, at 254 nm, the efficiency of photochemical conversion from benzvalene to benzene is very high ($\Phi^{253.7} = 0.715$).[26] Furthermore the reverse pathway occurs with a negligible quantum yield of ca. 0.01.[5] Under these conditions it should be expected that the benzvalene concentration would reach a steady value as observed in these experiments. The analogous fulvene to benzene photoisomerization has been shown to require vibrational excitation within the S_2 manifold.[27] In a matrix, the vibrational relaxation of any electronic state is rapid and the process would therefore be expected to be inefficient, leading to the observed linear production behavior for fulvene. In summary, it appears that both benzvalene and fulvene are primary products in the matrix photolysis of benzene at 253.7 nm, although the possibility that fulvene is also produced from benzvalene cannot be totally excluded.

Photoisomerization Mechanisms of Pyridine in Matrices. In a matrix it appears that the photolysis of pyridine results in isomerization as opposed to fragmentation as no ethyne, hydrogen cyanide, acrylonitrile, or cyclobutadiene could be detected.

The serial photolyses revealed that the products of photolysis must be primary as all temporal profiles for the various product IR bands were linear and did not tend to a limiting concentration as would be expected for intermediate species. Although the quantum yield of the $S_1 \rightarrow T$ crossing in pyridine may be as high as 0.30,[28] the first observation of a phosphorescent emission was

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(19) Bryce-Smith, D.; Gilbert, A.; Robinson, D. A. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 745.

(20) Cundall, R. B.; Robinson, D. A.; Pereira, L. C. *Adv. Photochem.* **1977**, *10*, 177.

(21) Gibson, E. P.; Rest, A. *J. Chem. Soc., Faraday Trans. II* **1981**, *77*, 109.

(22) Haller, I. *J. Chem. Phys.* **1967**, *47*, 1117.

(23) Phillips, D. *J. Chem. Phys.* **1967**, *46*, 4679.

(24) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309.

(25) Suijker, J. L.G.; Varma, C. A. G. O.; Huizer, A. H. *Chem. Phys. Lett.* **1984**, *167*, 496.

(26) Harman, P. J.; Kent, J. E.; O'Dwyer, M. F.; Griffith, D. W. T. *J. Phys. Chem.* **1981**, *85*, 2731.

(27) Kent, J. E.; Harman, P. J.; O'Dwyer, M. F. *J. Phys. Chem.* **1981**, *85*, 2727.

TABLE IV: Symmetry Correlations and Direct Products for D_{6h} in Various Site Symmetries

D_{6h}	D_{3h} ($c'_2 = X$)	D_{2h} ($\sigma_v \rightarrow \sigma_{yz}$) ($\sigma_h \rightarrow \sigma_{xy}$)	C_{2h} ($c_2 = Z$)	C_{2v} ($c_2 = Z$)
A_{1g}	A'_1	A_g	A_g	A_1
B_{2u}	A'_2	B_{3u}	B_u	B_1
B_{1u}	A'_1	B_{2u}	B_u	B_2
E_{2g}	E'	$A_g + B_{1g}$	A_g	$A_1 + A_2$
E_{1u}	E'	$B_{2u} + B_{3u}$	B_u	$B_2 + B_1$
D_{6h}	D_{3h}	D_{2h}	C_{2h}	C_{2v}
$B_{2u} \times E_{2g} = E_{1u}$	$A'_2 \times E' = E'$	$B_{3u} \times (Ag + B_{1g}) = B_{3u} + B_{2u}$	$B_u \times A_g = B_u$	$B_1 \times (A_1 + A_2) = B_1 + B_2$
$B_{1u}(S_2)$	A'_1	B_{2u}	B_u	B_2

TABLE V: Infrared Bands of Dewar Benzene in an Argon Matrix[15]

band, cm^{-1}	Dewar benzene assignment
705 (vs), 709 (vs)	=CH out of plane defm
793 (vvs), 795 (ws)	=CH out of plane bend
823 (s), 826 (s)	=CH out of plane bend
1268 (s), 1270 (s)	–CH bend

not reported until 1984.[29] A maximum was observed at λ = 450 nm with an associated lifetime and quantum yield of 1.2 ± 0.1 μs and 1.5×10^{-6}, respectively. Such low values strongly suggest the presence of an intrinsically rapid nonradiative decay channel from the T_1 state either by rapid $T_1 \rightarrow S_0$ intersystem crossing or indeed by the involvement of photochemical isomers. However Lemaire found no evidence for any triplet state, gas-phase chemistry in pyridine.[30] However the present study shows that photolysis in xenon leads to an enhancement in product band absorbances compared directly to results obtained in argon. This observation contrasts with the benzene experiments when all photochemistry was quenched in a xenon matrix. The results indicate strongly that a triplet state is involved in the isomerization process. This is the first report of T_1-state pyridine chemistry and contrasts to the gas-phase results of Lemaire, who did not observe any products from T_1. Since all product bands were enhanced, it is reasonable to assume that if more than one isomer is produced, then they all originate from the same triplet state. A low pressure study of gas-phase pyridine photolysis has shown the T_1 state to have unusual nonexponential, pressure-dependent decay characteristics.[31] The authors attributed this to the presence and interconversion of two triplet forms with widely different intrinsic lifetimes, brought about by strong pseudo-Jahn–Teller vibronic coupling between nearly degenerate $^3\pi\pi^*$ ($^3A_1$) and $^3n\pi^*$ ($^3B_1$) states. This results in a double minimum in the lowest triplet surface along an out of plane bending coordinate (b_1), yielding a vibrationally relaxed triplet state that is nonplanar in structure and that has quite different relaxation properties from the quasi-planar form generated by activation over the barrier between the two minima. It was further postulated that this nonplanar triplet may be involved in the photochemical generation of Dewar pyridine at 253.7 nm. In the cold matrix environment, rapid vibrational relaxation to such a "twisted" triplet state is expected.

Since, Wilzbach and Rausch observed only Dewar pyridine when they photolyzed liquid pyridine at 253.7 nm, it seems reasonable to propose that this isomer is produced in the present study (possibly in conjunction with azafulvene and azabenzvalene). If this is so, then similarities should be expected between the infrared spectrum of Dewar benzene (which is well characterized) and the post photolysis spectrum of matrix isolated pyridine. This assertion can be made because Dewar pyridine is structurally similar to Dewar benzene, and therefore similar vibrational modes should be present in its infrared spectrum.[32] For example, the most intense bands in the matrix spectrum of Dewar benzene are those associated with hydrogenic deformations as shown in Table V and indeed the after photolysis spectrum of pyridine does contain bands at 706.4, 730.4, 802.4, 810.3, 823.1, 1255.7, 1275.4 and 1278.3 cm^{-1}. These observations indicate that Dewar pyridine is the probable product of photolysis. An ab initio calculation of its infrared spectrum will be the subject of a future report.

Conclusion

Dewar benzene has been shown to be a primary product of benzene photolysis in low temperature argon matrices at 253.7 nm. This is the first observation of Dewar benzene formation at this wavelength. A mechanism is proposed involving S_1–S_2 state mixing induced by the matrix environment. Furthermore, in xenon matrices all of the photochemistry is quenched. Fulvene and benzvalene are both primary photolysis products; however benzvalene undergoes photoinduced reisomerization to benzene after prolonged photolysis. The analogous photoisomerization of pyridine produces only primary product(s) originating from a triplet state, probably T_1. Analysis of the infrared product bands points to this isomer being Dewar pyridine although other isomers cannot be ruled out.

This is the first observation of triplet state chemistry in pyridine. It is a result that explains why the measured quantum yield of phosphorescence is low and the phosphorescence lifetime is short.

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(28) Sushida, K.; Fujita, M.; Yamazaki, I.; Baba, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2228.

(29) Sushida, K.; Fujita, M.; Takemura, T.; Baba, H. *Chem. Phys.* **1984**, *88*, 221.

(30) Lemaire, J. *J. Phys. Chem.* **1967**, *71*, 612.

(31) Selco, J. I.; Holt, P. L.; Weisman, R. B. *J. Chem. Phys.* **1983**, *79*, 3269.

(32) Bellamy, L. J. *The infrared spectra of complex molecules*; John Wiley & Sons: New York, 1975.