The Vacuum Ultraviolet Photolysis of Benzene[1,2]

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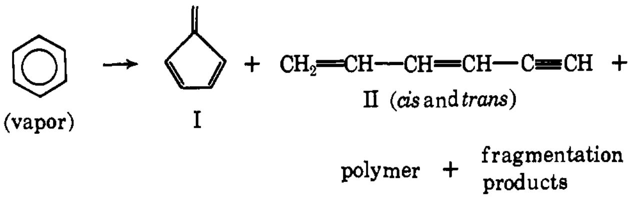
Abstract: The vacuum ultraviolet photochemistry of benzene vapor has been investigated in detail, including the identification of major and minor photoproducts, the determination of quantum yields for major products, and the investigation of the variation of the quantum yields with pressure. The major volatile products of the vapor photolysis were found to be fulvene and *cis*- and *trans*-1,3-hexadien-5-yne. The effects of pressure on the quantum yields for fulvene and dienyne production were studied in the pressure range 1–200 mm. The quantum yields for both of these compounds fell off at high as well as low pressures, and extrapolated to zero at zero pressure. The total quantum yield ($\phi_{\text{fulvene}} + \phi_{\text{dienyne}}$) passed through a maximum value at about 60 mm. The formation of fulvene was favored at higher pressures, and the 1,3-hexadien-5-ynes were favored at lower pressures. A mechanism utilizing a vibrationally excited ground electronic state of benzene is proposed. The vacuum ultraviolet photolysis of liquid benzene produced fulvene, benzvalene, and dewar benzene. This photoreaction is thought to proceed through vibrationally excited upper electronic states of benzene.

Benzene molecules excited to their second or third singlet states have been shown to lose energy by highly efficient nonradiative processes.[4] The importance of these processes, as determined by emission measurements, increases with decreasing excitation wavelength and in going from liquid to vapor phase.[4] Thus, for benzene vapor excited at 1849 Å, virtually no emission is observed, which suggests the occurrence of either (or both) photochemical processes or radiationless transitions to the ground electronic state. If photochemical processes are solely responsible for the loss of excitation energy, then the quantum yield for benzene disappearance would be expected to approach unity in photolyses of benzene at very low pressures. Early data concerning the vacuum ultraviolet photolysis of benzene vapor[5] indicated that the quantum yields for the formation of hydrogen and acetylene were much smaller than unity. These results, however, were obtained using only the classical analytical methods available at that time, which limited product characterization to readily identifiable stable compounds which could be easily separated from benzene. The possibility therefore remained that the application of modern analytical techniques to this problem might reveal the presence of interesting photoproducts such as, perhaps, benzene valence isomers. More recent investigations[6,7] have shown that the quantum yield for benzene disappearance does indeed approach a value close to unity at low pressures, and small yields of photoproducts have been reported by several groups.[2,6–8]

On the basis of these considerations, we have undertaken a study of the vacuum ultraviolet photolysis of benzene, with primary emphasis on the identities of the products and the quantum yields for product formation, rather than on the disappearance of benzene.

Results

Vapor Phase Vacuum Ultraviolet Photolyses. Irradiation of benzene vapor in the region of the second and third absorption bands (~2000 and ~1850 Å, respectively) resulted in a complex mixture of hydrocarbons, in addition to polymer on the lamp window. The major volatile products were benzene isomers, but reduced and alkylated benzenes, biphenyl, dihydrobiphenyls, and higher reduced polyphenyls were also present in low concentrations. Low molecular weight products such as methane, ethane, ethylene, and acetylene have been reported by Foote, Mallon, and Pitts.[6] At initial benzene pressures greater than about 15 mm, or in the presence of added inert gas, the major volatile photoproduct was fulvene (I), with a mixture of the isomeric 1,3-hexadien-5-ynes (II) as the second most abundant product.[9] The hexadienynes, especially at lower pressures, were usually present as equal concentrations of the *cis* and *trans* isomers. It is conceivable that this equivalence results from the known benzene-sensitized photoisomerization of olefins,[10] although the electronic states of benzene thought to be involved in these isomerizations are probably unimportant in the vacuum ultraviolet photolysis (*vide infra*). (Secondary photoprocesses are unlikely, in view of the low conversions in most experiments.) It is also possible that the excited state partitions into equal amounts of the *cis* and *trans* isomers.



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(1) The authors gratefully acknowledge financial support from the National Science Foundation.

(2) Two preliminary reports of this work have previously appeared: (a) H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *J. Amer. Chem. Soc.*, **89**, 162 (1967); (b) H. R. Ward and J. S. Wishnok, *ibid.*, **90**, 1085 (1968).

(3) NASA Trainee, 1965–1968.

(4) C. L. Braun, S. Kato, and S. Lipsky, *J. Chem. Phys.*, **39**, 1645 (1963).

(5) J. E. Wilson and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **63**, 3025 (1941).

(6) J. K. Foote, M. H. Mallon, and J. N. Pitts, Jr., *ibid.*, **88**, 3698 (1966).

(7) K. Shindo and S. Lipsky, *J. Chem. Phys.*, **45**, 2292 (1966).

(8) L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **89**, 1030 (1967).

(9) Kaplan and Wilzbach[8] have also observed fulvene in the 1849-Å photolysis of benzene vapor and have suggested the possibility of compounds II being present in the product mixture.

(10) (a) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 1151 (1966); (b) M. Tanaka, M. Kato, and S. Sato, *Bull. Chem. Soc. Jap.*, **39**, 1423 (1966).

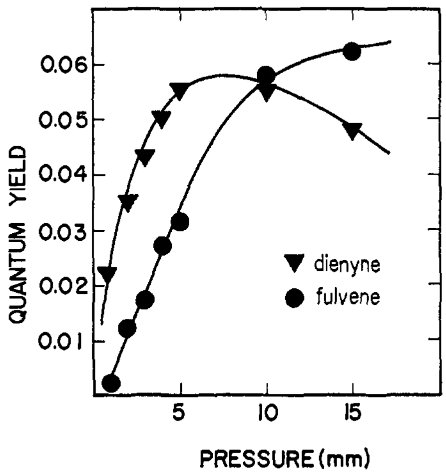


Figure 1. Variation of fulvene and total dienyne quantum yields with pressure.

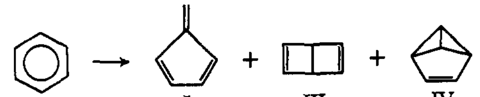
The fulvene–dienyne ratio was found to be strongly pressure dependent, and the dienynes began to predominate at pressures lower than about 10 mm. At any given pressure, however, the fulvene–dienyne ratio was independent of photolysis time, which indicated that neither of these compounds was a secondary product arising *via* the other. The total (fulvene + dienyne) conversion per unit time increased as irradiation times were decreased to 0.5 min. There was no indication that the values for the quantity (conversion/time) approached zero, which suggested that fulvene and dienyne were primary photoproducts. Photolysis times shorter than 0.5 min were not investigated, so this evidence cannot rule out the establishment of a steady state in times less than this. Figure 1 illustrates the variation of the total dienyne quantum yield and the fulvene quantum yield with pressure. The points in Figure 1 are for photolyses of pure benzene in the pressure range 1–15 mm. Although the quantum yields for both compounds decreased sharply at pressures below 1 mm, the dienyne–fulvene ratio increased from ~1 at 10 mm to ~10 at 1 mm. If the pressure was increased above 15 mm by the addition of nitrogen, the dienyne quantum yield appeared to decrease steadily, while the fulvene quantum yield passed through a maximum ($\phi_{\max} = 0.08 \pm 0.02$) at about 80 mm. At 200 mm (the highest pressure studied), ϕ_{fulvene} was 0.06 ± 0.02 and ϕ_{dienyne} was 0.035 ± 0.01. (It is not obvious that the quantum yields reported in this work can be compared, on an absolute basis, with those reported[6,7] for the 1849-Å photolysis.)

Although quantitative studies of fragmentation products (methane, ethane, etc.) were not carried out, the relative rate of formation of these compounds was observed to increase sharply as the pressure was lowered, and thus qualitatively paralleled the disappearance quantum yield for benzene.[6,7] At the lowest pressure investigated (1 mm), the total yield of fragmentation products was less than 5% of that for the dienynes, which were the major observable products at this pressure. It was impossible to measure directly the amount of polymeric material formed in these photolyses. From crude estimates of the relative amounts of polymer formed during the photolyses reported in Figure 1, it was obvious that the quantum yield for polymer formation increased significantly as the pressure was lowered. Although no direct quantitative information concerning the polymer is available, the fact that the quantum yields for volatile products decrease at very low pressures while the benzene disappearance quantum yield increases[6,7] confirms that polymer is by far the major product of this photolysis.

Minor products ($\phi < 0.005$) of the vapor photolysis included reduction products, such as the cyclohexadienes, and the 1,3,5-hexatrienes, in addition to the higher molecular weight products mentioned earlier.[11-13] Several other minor products were present in the photolysate, but were not identified. Fulvene and 1,3-hexadien-5-yne were typically present to the extent of about 0.05–0.1% of recovered benzene. Products with concentrations of the order of 0.002% of recovered benzene were readily detected by flame-ionization gas chromatography, and could usually be identified by relative retention times and mass spectra, if they were known compounds and if they could be cleanly resolved by gas chromatography. This latter requirement was the principal obstacle to product characterization. No "major" ($\phi > 0.01$) products (except polymer) remain unidentified.

The necessity of a hydrogen migration during the formation of fulvene and 1,3-hexadien-5-yne suggested the possibility of an intermolecular pathway for the isomerization of benzene to either of these compounds. To clarify this point, a mixture of benzene and benzene-d_6 was photolyzed under typical conditions. There was no evidence of label exchange in the fulvene and dienyne obtained from this reaction.

Liquid Phase Vacuum Ultraviolet Photolyses. With the exception of small amounts of biphenyl and polymer, only benzene isomers were observed in the liquid phase photolysate. Dewar benzene (III) was formed,[14-18] in addition to benzvalene (IV)[19] and fulvene (I). The quantum yields for this photolysis were 0.03 ± 0.005, 0.012 ± 0.003, and 0.006 ± 0.001 (IV, I, and III, respectively).



(liquid) I III IV

Discussion

When benzene is excited with vacuum ultraviolet radiation in the 2000–1600-Å region, at least seven

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(11) In some respects, the minor products were similar to the products from the photolysis of benzene vapor at 1470[12,13] and 1236 Å.[12] There is, however, lack of agreement concerning the details of these photolyses which must be resolved before rigorous comparisons of these systems with ours are in order. For example, the 1470-Å photolysis has been investigated by two groups.[12,13] In one case,[13] biphenyl was not observed as a photoproduct, and major conclusions were based on the absence of this compound; the second group of investigators[12] reported the formation of biphenyl with a quantum yield comparable to those of other photoproducts such as hydrogen, acetylene, ethylene, etc.

(12) R. R. Hentz and S. J. Rzad, *J. Phys. Chem.*, **71**, 4096 (1967).

(13) W. M. Jackson, J. L. Faris, and B. Donn, *ibid.*, **71**, 3346 (1967).

(14) There have been several reports of photoisomerization of substituted benzenes to the corresponding dewar forms.[15-18]

(15) I. Haller, *J. Amer. Chem. Soc.*, **88**, 2070 (1966); *J. Chem. Phys.*, **47**, 1117 (1967).

(16) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965).

(17) E. E. van Tamelen and S. P. Pappas, *ibid.*, **84**, 3789 (1962).

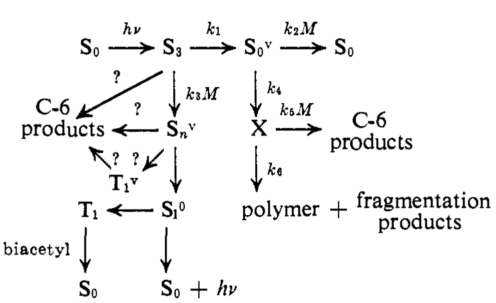
(18) E. M. Arnett and J. M. Bollinger, *Tetrahedron Lett.*, 3803 (1964).

(19) Tricyclo[3.1.0.0^{2,6}]hex-3-ene.

molecular electronic states become accessible, either by direct excitation or by internal conversion or intersystem crossing from the initial excited states. In this wavelength region, the initial excitation will almost certainly be to one of the two upper singlet states, S_2 or S_3. Of these two states, S_3 ($^1E_{1u}$) is more likely in our system since the transition to S_3 is more strongly allowed and because the most intense emission lines from the oxygen discharge (see Experimental Section) overlap closely with the maximum absorption of the $S_0 \rightarrow S_3$ band.[20,21] Although the *initial* excitation is probably to S_2 or S_3, the observed pressure dependence of the benzene-disappearance quantum yield[7] and the product-formation quantum yield demonstrate that neither of these states goes directly to photoproducts, since both are too short lived[4] to be affected by collisions. This has been pointed out by Shindo and Lipsky,[7] who present strong arguments, based on spectroscopic evidence, that the remaining possible electronic excited states of benzene—S_1, T_1, T_2, and T_3—also are probably unimportant in the vacuum ultraviolet photolysis of benzene vapor. They therefore propose that the photochemical destruction of benzene vapor proceeds *via* a vibrationally excited ground electronic state ($S_0{}^v$) of benzene. The results reported in this work are compatible with this proposal and, indeed, offer strong experimental support for it.[22,23] Deactivation of upper electronic states to the ground state (without change in multiplicity) is generally believed to proceed through each intermediate state in turn.[24] Although the transitions $S_n \rightarrow S_1$ usually occur rapidly, the $S_1 \rightarrow S_0$ transition is much less favorable, which corresponds to a relatively long lifetime for S_1 during which emission or intersystem crossing may occur.[24] In benzene, however, this path of decay ($S_3 \rightarrow S_2 \rightarrow S_1$) is contraindicated by the very low emission and biacetyl-sensitization quantum yields which have been observed over wide pressure ranges in the 1849-Å photolysis.[4] The alternative, a rapid crossover from the initial excited state (probably S_3) into an upper vibrational level of the benzene ground state ($S_0{}^v$), is consistent with the spectroscopic observations. This crossover would then require that simple collisional deactivation of excess vibrational energy in the S_0 manifold be the major process competing with photochemistry. The slight increase in emission and biacetyl sensitization in the liquid phase[4] indicates that a relatively inefficient collisional deactivation to S_1 can also occur in the presence of very high concentrations of collisional deactivators. A generalized reaction scheme for the photochemical destruction of benzene, and the low quantum yield photophysical processes, is shown below (M = total concentration). The low emission and biacetyl-sensitization quantum yields demand that k_1 be much larger than k_3M for virtually all values of M, and the low quantum yields[7] for benzene disappearance at moderate pressures [ϕ(-benzene) <0.1 for $P > 3$ mm] indicates that k_2M is much greater than k_4 except at very low pressures. This reaction scheme leads to an equation of the form

$$\phi = 1 - k_2M/(k_2M + k_4)$$

for the disappearance of benzene at low pressures. Using the values of Shindo and Lipsky[7] for the benzene-disappearance quantum yields at several pressures, the ratio k_4/k_2 can be shown to be of the order of 10^{-5}–10^{-6}, *i.e.*, that k_2M becomes relatively important as the pressure is raised to a few millimeters ($M \simeq 5.4 \times 10^{-5}$ mol/l. at $P = 1$ mm).



The nature of the excited state(s) X in this reaction scheme cannot be definitely established on the basis of information currently available. The most straightforward possibility, however, is a conversion of the vibrationally excited benzene ground state into vibrationally excited product ground states. (Only fulvene

$$S_0{}^v(\text{benzene}) \longrightarrow S_0{}^v(\text{fulvene}) + S_0{}^v(\text{dienyne})$$

and the dienynes will be considered individually; all other photoproducts will be considered together, with the assumption that polymer is the most important of these.) This proposal predicts that the product quantum yields will be affected by two separate pressure dependences, both of which are highly efficient, and which operate in opposite directions. The first of these is the effect of pressure on $S_0{}^v$(benzene) in which increasing pressure is expected to lower the quantum yield for the formation of $S_0{}^v$(product). On the other hand, increasing pressure should favor the analogous deactivation of $S_0{}^v$(fulvene) and $S_0{}^v$(dienyne) to form the respective stable molecules. At low pressures, then, the low quantum yields for fulvene and dienyne may be attributable to the formation of fragmentation products and polymer from $S_0{}^v$(fulvene) and $S_0{}^v$(dienyne), *i.e.*, $k_5M < k_6$. The low values for ϕ(fulvene) and ϕ(dienyne) at higher pressures may be a result of the efficient bimolecular deactivation of $S_0{}^v$(benzene) to stable benzene ($k_2M > k_4$). At very low pressures the benzene disappearance quantum yield would be expected to approach unity (*i.e.*, $k_2M \rightarrow 0$), while the fulvene and dienyne quantum yields approach zero. These predictions agree very well with experimental data.

This proposal also is supported by the observations of Heffernan and Jones,[25] who have shown that benzene and fulvene are formed in the pyrolysis of 1,3-hexadien-5-yne, and by the results of shock-tube experiments[26] in which fulvene and probably the 1,3-hexadien-5-ynes are formed in the shock-tube pyrolysis of benzene. Both of these results demonstrate that the isomeric

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(20) A third possible initial excited state is a low-lying Rydberg state, which is apparently isoenergetic with the $S_0 \rightarrow S_3$ absorption for benzene.[21] Rydberg states, however, are not well understood for polyatomic molecules, and it is therefore difficult to consider these states in connection with the details of any complex photochemical process.

(21) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, D. van Nostrand and Co., Inc., Princeton, N. J., 1966, p 560.

(22) Vibrationally excited ground electronic states have also been proposed in connection with the vacuum ultraviolet photolysis of *o*-xylene,[23] and in the 1470- and 1236-Å photolysis of benzene.[11]

(23) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 2367 (1967).

(24) S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.*, **3**, 269 (1965), and references therein.

(25) M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966).

(26) H. R. Ward and J. S. Wishnok, unpublished results.

products in the vacuum ultraviolet vapor phase photolysis are accessible from one another *via thermal* pathways.

The identification of the excited state(s) which lead(s) to the products observed in the vacuum ultraviolet photolysis of liquid benzene is more difficult. The fluorescence and biacetyl sensitization quantum yields in the liquid phase are low,[4] as predicted by the reaction scheme just discussed. They are, nonetheless, higher than those observed in the vapor phase, indicating that the S_1 and T_1 states are being populated to some extent in the liquid system. Since product quantum yields are also low, the possibility that the photochemistry proceeds *via* electronic excited states cannot be rejected. Theoretical considerations,[27,28] based on correlations of orbital symmetries, predict that dewar benzene and benzvalene should arise from excited electronic states, rather than the ground state, of benzene. The benzene T_1, S_1, S_2, and S_3 states are predicted to satisfy the symmetry requirements for the photochemical conversion of benzene to one or the other of the observed valence isomers. Comparisons of the vacuum ultraviolet liquid phase photolysis of benzene with near-ultraviolet photolyses, however, indicate that S_1 and perhaps T_1, rather than the higher states, are the states which may lead to benzvalene. (The fulvene observed in the liquid phase photolysis may be thought of as arising by the same pathway as in the vapor phase photolysis, but it is also possible that this compound is formed from benzvalene *via* an acid-catalyzed rearrangement.[29] This point has not yet been investigated in detail.) Benzvalene is a common product of the 2537-Å photolysis[30] and the liquid phase vacuum ultraviolet photolysis of benzene. If a common intermediate is assumed to be present in both systems, then the only electronic states available for consideration are S_1 and S_0. (Benzvalene has been shown not to arise from T_1 in the 2537-Å photolysis of benzene vapor.[31]) The importance of vibrational excitation in addition to electronic excitation in order for benzvalene to be formed is demonstrated by the strong pressure dependence of the benzvalene quantum yield (benzvalene is most readily observed in liquid phase photolyses[2b,30] and at high pressures in the vapor phase[31]), and the fact that photoisomerization of benzene to benzvalene is enhanced by increasing temperatures.[30,32] Thus, in the 2537-Å photolysis of benzene in hexadecane,[30] benzvalene probably arises from an upper vibrational level of either S_1 or S_0, and it is not unreasonable to suggest that the same state is responsible for the formation of benzvalene in the vacuum ultraviolet photolysis of liquid benzene.

The photochemical transformation of benzene to dewar benzene has been treated theoretically by several workers.[27,28,32] Bryce-Smith and Longuet-Higgins[27] have proposed that dewar benzene may arise from a triplet biradical which is formed from the benzene T_1 state, and Hoffmann and Woodward[28] suggest that photochemical pathways from benzene to dewar benzene are allowed from benzene excited states with $B_{1u}(T_1, S_2)$ or $E_{1u}(S_3)$ symmetry. No systematic studies relevant to these predictions have been reported, although it has been shown[29] that concurrent radiation with 2537-Å light does not affect the formation of dewar benzene in the 1849-Å photolysis of liquid benzene. This indicates that the *lower vibrational levels* of the benzene T_1 state are not involved in this transformation. A vibrationally excited T_1 state, as proposed by Bryce-Smith,[32] cannot be excluded. The liquid phase vacuum ultraviolet photolysis of benzene may conceivably be related to the near-ultraviolet photolysis of hexafluorobenzene vapor.[15] The mechanistic details of the latter system, however, have not been clearly established. The hexafluoro dewar benzene is apparently formed *via* a singlet state at wavelengths in the 2480-Å region, but triplets may be important at longer wavelengths.[15] The information presently available is insufficient to allow any firm conclusions to be drawn concerning the nature of the excited state leading directly to dewar benzene.

Experimental Section

Vacuum Ultraviolet Photolyses. Most of the qualitative photolyses were carried out in an oxygen discharge reaction system, which has been described in detail in a previous publication.[23] This lamp emitted a series of sharp lines extending from 2000 to 1650 Å, with the two most intense bands near 1800 Å. The emission overlapped nicely with the second and third absorption bands of benzene. The high output of the lamp ($\sim 10^{17}$ quanta/sec) proved especially useful for obtaining relatively high conversions in short irradiation times.

Quantitative photolyses (*e.g.*, quantum yield variations with pressure) were usually carried out in a somewhat different system, shown schematically in Figure 2. Chamber A was the light source and contained oxygen ($P = 200\ \mu$) in which an electrodeless discharge was sustained by microwave power (Raytheon PGM 100, 2450 Mc). This chamber was fitted at the outlet with a T tube through which the oxygen was slowly passed, thus creating a semistatic system. (Sealed lamps operated only for short periods.[23,33]) Chamber C contained the sample being irradiated, and chamber B insulated the reaction chamber from the high temperatures of the discharge. A liquid nitrogen boiler, operated from a variac, sustained a flow of cool nitrogen through chamber B. The temperature jacket, D, could be used for precise temperature control or for obtaining elevated temperatures. The system was constructed of fused silica except for the windows (W_1 and W_2), which were of Suprasil (Englehard Industries). For liquid phase photolyses, the lamp was inverted, which allowed the use of small amounts of reactant ($\sim 175\ \mu$l), thus minimizing dilution of product by unreacted starting material. This lamp emitted approximately 10^{15} quanta/sec, as determined by oxygen actinometry.[34]

For qualitative photolyses, the desired volume of benzene (10–30 μl) was placed in a small trap connected to the reaction chamber with standard taper joints. The system was attached to the vacuum line, the benzene cooled to 77°K, and the reaction chamber evacuated. The benzene was degassed by several freeze–thaw cycles and, finally, the system was sealed under vacuum (vacuum stopcock) and removed from the line. The lamp was placed in the microwave resonant cavity, and the benzene allowed to warm to room temperature, filling the chamber with vapor. The photolysis was then carried out for the desired amount of time, usually between 0.5 and 3.0 min. For quantitative experiments, the lamp was joined to the vacuum line and evacuated. The manifold was sealed off, and degassed benzene from a cooled reservoir was allowed to expand into the manifold and reaction chamber. The reaction chamber was then closed off and the photolysis carried out as described above. Pressures were read directly from Bourdon gauges (Wallace and Tiernan Co.). In some instances, pressures were obtained by

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[27] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

[28] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[29] K. E. Wilzbach, personal communication.

[30] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1031 (1967).

[31] L. Kaplan and K. E. Wilzbach, personal communication.

[32] D. Bryce-Smith, *Pure Appl. Chem.*, submitted for publication.

[33] J. S. Wishnok, Ph.D. Thesis, Brown University, 1968.

[34] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 782, and references therein.

Table I. Relative Retention Times of C_6H_6 Isomers

	Relative retention time (benzene = 1.00)				
Compound	UCON (40°)	FFAP (40°)	Squalane (30°)	TCEP (30°)	DDP-TEA[a] (30°)
cis-1,3-Hexadien-5-yne	1.37	1.45	0.73	1.15	*b*
trans-1,3-Hexadien-5-yne	1.56	1.62	0.78	1.35	*b*
Fulvene	0.90	*c*	0.77	0.89	*b*
Dewar benzene	0.45	*b*	0.63	*b*	*b*
Benzvalene	*b*	*b*	*b*	*b*	0.80

[a] Didecyl phthalate–triethanolamine.[28] [b] Not determined. [c] Did not elute.

equilibrating benzene vapor with solid or liquid benzene at known temperatures.[35]

After each photolysis, the polymer was removed from the lamp window by washing with dilute HF. The lamp was then rinsed with water, soaked in dilute NaOH for about 1 hr, and then rinsed again with water. In the liquid phase photolyses, the final rinse was with very dilute NaOH. The water was then removed to leave a thin coating of NaOH on the inner lamp surface. Except for the apparent isomerization of benzvalene to fulvene in the liquid phase photolysis, the nature of the lamp surface had little apparent effect on the photolyses.

The product mixtures were analyzed principally by gas chromatography, and identifications were usually made by comparison of retention times of products with the retention times of known compounds on several columns. A gas chromatograph–mass spectrometer[36] combination was available, and molecular weights and (in some instances) cracking patterns were obtained for many of the products with this combination. Under normal operating conditions, all of the C_6H_6 isomers which were studied gave mass spectra qualitatively indistinguishable from that of benzene.

In addition, fulvene from the vacuum ultraviolet vapor phase photolysis, and dewar benzene from the vacuum ultraviolet liquid phase photolysis were isolated by microscale preparative gas chromatography. Sufficient fulvene was obtained to allow conventional characterization by infrared, ultraviolet, and nmr spectroscopy. The dewar benzene was collected in pyridine and was observed to thermally isomerize to benzene.[37]

No single chromatographic system was found which would cleanly separate all of the C-6 hydrocarbons formed in these photolyses. The following columns, however, proved adequate to analyze for most products: 10 ft × 0.125 in. aluminum column containing 15% TCEP on 100–120 mesh Chromosorb P; 15 ft × 0.125 in. aluminum column containing 25% UCON 50HB 100 on 100–120 mesh Chromosorb W; 15 ft × 0.125 in. aluminum column containing 15% Squalane on 100–120 mesh Chromosorb W; 3 ft × 0.125 in. aluminum column containing 15% FFAP on 100–120 mesh Chromosorb W; 3 ft × 0.125 in. aluminum column containing 5% SE-30 on 100–120 mesh Chromosorb W; 3 ft × 0.125 in. aluminum column containing 15% SF-96 on 100–120 mesh Chromosorb W. In addition to these a 10 ft × 0.125 in. aluminum column containing 5% didecyl phthalate and 2% triethanolamine on 100–120 mesh Chromosorb W was used to analyze for benzvalene.[28] The isolation of fulvene and dewar benzene was accomplished on columns of varying length 0.25 in. diameter aluminum containing 25% UCON 50HB 100 on 100–120 mesh Chromosorb W (see Table I).

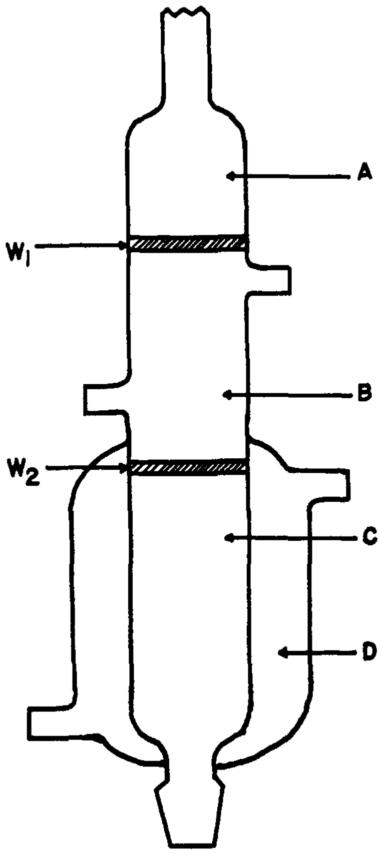

Figure 2. Vacuum ultraviolet reaction system: A, discharge chamber; B, temperature buffer; C, reaction chamber; D, temperature jacket; W_1, W_2, windows.

Mass spectral parent ion analysis at reduced ionizing voltage was used to determine the extent of label exchange in the photolysis of benzene–benzene-d_6 mixtures.

Materials. Fisher Research grade benzene was purified by repeated crystallizations until virtually no impurities were detectable by flame-ionization gas chromatography. Impurities present to the extent of 1 part per million would have been readily detectable. Fulvene,[38] dewar benzene,[37] benzvalene,[30] and 1,3-hexadien-5-yne[39] were prepared by known methods for use as gas chromatographic standards. Perdeuteriobenzene (E. Merck A. G.) was obtained from Brinkmann Instruments, Inc., and used without further purification.

Acknowledgment. We are grateful to Dr. Kenneth Wilzbach and Dr. Louis Kaplan for making their results available to us prior to publication.

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