label (92 c.p.m. *vs.* 98 c.p.m. for a blank solution). Similar results were obtained when tritiated water was added to a solution of polyxylenol under polymerizing conditions.

2,6-Dimethylanisole-3-H^3.—A solution of 0.15 g. of 2,6-xylenol-3-H^3 (3.54×10^9 d.p.m./mole) and 1.05 g. of ordinary 2,6-xylenol was dissolved in 5.5 ml. of 2 *N* sodium hydroxide solution. The temperature was kept below 40° while 1.26 g. of dimethyl sulfate was added dropwise with stirring. An additional 3 ml. of 2 *N* sodium hydroxide solution was then added followed by 0.63 g. of dimethyl sulfate. The reaction mixture was heated for 30 min. on a steam-bath. Upon cooling, it was extracted with two 10-ml. portions of diethyl ether. The extracts were dried over sodium sulfate and distilled. A colorless oil was collected; b.p. 82.5–84° (30 mm.), yield 1.1 g. (80%), S.A. 4.44×10^8 d.p.m./mole.

Polymerization in the Presence of 2,6-Dimethylanisole-3-H^3.—To the standard polymerization mixture described previously was added 0.54 g. (0.004 mole) of 2,6-dimethylanisole-3-H^3 together with the 2,6-xylenol (0.49 g.). The resulting polymer was isolated and purified in the usual manner. The tritium content of this polymer was too low (49.5 c.p.m./mg.) to be distinguished as significantly above the natural background (47 c.p.m./mg.)

Test of "Quinol Ether Rearrangement."[2d]—The polymerization procedure described above was utilized. One-half (9.75 ml.) of the reaction mixture was withdrawn and treated in the usual manner to give 0.22 g. (92%) of purified product, [η] 0.93 dl./g.

To the remaining reaction mixture was added 0.245 g. (0.002 mole) of 2,6-xylenol and the reaction was resumed with the development of an orange color. After 50% of the theoretical oxygen was absorbed, the reaction was quenched by the addition of 15 ml. of 1 *N* hydrochloric acid. The product was isolated as before, yielding 0.21 g. (88%) of polymer, [η] 0.75 dl./g.

The filtrate from this second portion was steam distilled until all volatile material had been removed. The residue consisted of a brown gum (0.20 g., 85% based on the 0.245 g. of additional xylenol), which was not polymeric, [η] 0.02 dl./g.

[Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Conn., and Department of Chemistry, The University of Michigan, Ann Arbor, Mich.]

The Absorption Spectrum of Gaseous Benzyne

By R. Stephen Berry,[1a] G. Neil Spokes[1a] and Martin Stiles[1b]

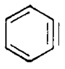
Received March 23, 1962

Flash photolysis has been carried out on thin solid films of two substances known to give benzyne under other conditions. Transient and final product ultraviolet gas phase spectra have been recorded and at least one reaction has been observed, with butadiene. On the basis of the observed final products, the reactions and the appearance of a transient continuous spectrum, it is concluded that gaseous benzyne is produced and that it probably is responsible for the transient absorption spectrum.

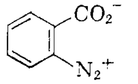
I. Introduction

The molecular fragment 1,2-dehydrobenzene (hereinafter called benzyne) (I) has been the subject of intensive study in its role as an intermediate in organic reactions. The chemistry of benzyne has been reviewed recently.[2-5] In contrast to our present extensive knowledge of the chemical properties of benzyne in solution, very little headway has been made in the examination of the species itself, either in terms of its physical properties or of its chemical reactions in the gas phase. Some preliminary theoretical estimates have been made in order to get a qualitative idea of the structure and properties of benzyne.[6,7] No detailed calculations have been reported which attempt to investigate electronic energy states and the relation between the structure of benzyne and that of benzene, for example.

The work described here was, in large part, suggested by the recent discovery of two new paths for the apparent production of benzyne. These paths are based on the precursors benzenediazonium-2-carboxylate[8] and on *o*-iodophenylmercury compounds.[9] Benzenediazonium-2-carboxylate (II) leads to benzyne under very mild conditions; it is very sensitive to heat or shock, detonating when warmed quickly or struck. It is a strong absorber of ultraviolet light, and is non-volatile.

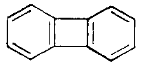


I

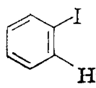


II

These observations led to a series of experiments in which solid films of **II** were flash-photolyzed and the ultraviolet absorption spectra of transient and final products were observed. The results, already reported in part in a preliminary communication,[10] indicated the presence of gaseous benzyne, because one could observe the formation of biphenylene (III), the dimer of benzyne, in the gas phase. Moreover the transient spectrum which was recorded clearly differed from that of ordinary biphenylene, and was tentatively assigned as the spectrum of benzyne.



III



IV

Since that time, similar methods have been applied in the flash photolysis of *o*-iodophenylmercuric iodide (IV), a compound whose role as a benzyne precursor had been shown by Wittig and Ebel.[9] The results obtained from these experiments have provided strong support for attributing the transient spectrum to benzyne.

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[1] (a) Yale University; (b) University of Michigan.

[2] (a) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); (b) J. D. Roberts, *Chem. Soc. (London) Spec. Publ. No.* **12**, 115 (1958).

[3] R. Huisgen, Chapter 2 in "Organometallic Chemistry," H. H. Zeiss, ed., Reinhold Publishing Corp., New York, N. Y., 1960, p. 36.

[4] J. F. Bunnett, *J. Chem. Ed.*, **38**, 278 (1961).

[5] H. Heaney, *Chem. Revs.*, **62**, 81 (1962).

[6] C. A. Coulson, *Chem. Soc. (London) Spec. Publ. No.* **12**, 85 (1958).

[7] H. G. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961).

[8] M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960).

[9] G. Wittig and H. F. Ebel, *Angew. Chem.*, **72**, 564 (1960).

[10] R. S. Berry, G. N. Spokes and R. M. Stiles, *J. Am. Chem. Soc.*, **82**, 5240 (1960).

We propose here to discuss the following topics: the details of methods used to obtain the results outlined previously; more precise and quantitative spectroscopic measurements than those reported earlier for photolysis of II; the results of analogous photolyses of IV; and, finally, such results we have so far obtained on gas-phase, benzyne-like reactions which bear on the identification and characterization of gaseous benzyne itself. We shall reserve extensive discussion of gas-phase reactions of benzyne for later publication. The following section describes the experimental details of apparatus and methods by which photolyses were carried out and absorbances derived from spectrograms. The third section contains a discussion of experimental results from photolyses of II and IV, alone, and with both inert and reactive gases added. The last section presents the conclusions we draw from the material of the previous sections, including a spectral curve attributed to benzyne.

II. Experimental

A. **Apparatus.**—The flash photolysis apparatus is shown schematically in Fig. 1. Its essential parts are the photolysis lamp, absorption cell, spectral flash, a variable-delay to control the interval between photolytic and spectral flashes, and a medium quartz spectrograph. A glass-prism instrument was used for visible and infrared work.

The absorption cells and lamp tubes are of clear fused silica. Sample cells (1.6–1.8 cm. i.d.) and photolysis flash tubes (1.5 cm. i.d.) have facilities for evacuation. Absorption cells have fused silica end windows sealed on with Apiezon W wax. Photolysis flash tubes are fitted with brass screw-on fittings with O-ring seals; these hold cylindrical tungsten electrodes *ca.* 1 cm. diam. and 2 cm. long. The photolysis tubes contain argon at a pressure just high enough to prevent spontaneous breakdown at 6 kv. The lamp is fired when a Tesla discharge is applied to an external electrode near the middle of the silica tube. The ringing frequency of the circuit is approximately 100 kc. and most of the energy is dissipated in the first 20 microseconds.

The spectrum flash is a low-pressure capillary lamp somewhat similar to that described by Ramsay.[11] It consists of a fused silica tube (2 mm. i.d., 5 cm. long) with aluminum screw-on end electrodes with O-ring seals. Because of considerable erosion of the aluminum, it is convenient to have replaceable cylindrical, tubular aluminum inserts in the electrodes; these act as seats for the ends of the capillary and can be replaced easily after 10 to 20 flashes. The lamp is pumped continuously; a pinhole leak keeps the air pressure in the capillary at about 1 mm. Capacitors totaling 24 microfarads charged to 3.5–4 kv. give sufficient energy to permit a very satisfactory spectrum to be recorded in a single flash. About 90% of the light is emitted in 20 microseconds. The lamp is discharged by application of a positive pulse to the grid of a hydrogen thyratron tube (5C22) in series with the capacitors and flash lamp. An oscilloscope (Tektronix 533), triggered by the discharge of the photolysis flash, provides a pulse which actuates a variable delay which in turn generates the firing pulse of the thyratron. The lower limit of the total delay is 20 microseconds. (The time reported previously[10] as 10.8 μsec. was found to be in error by approximately 10 μsec.)

The light from the spectral flash is passed the length of the sample tube as a slightly convergent beam, and is focused on the spectrograph slit.

B. **Procedure.**—Solids to be photolyzed were dissolved or suspended in solvents which could be removed easily. About 0.5 ml. of liquid was deposited onto the bottom of the sample cell near the center of the tube. The solvent was then pumped away or, in the case of ether, evaporated in a nitrogen stream. Cells were then evacuated to pressures of 20 μ or less, usually below 10 μ. Photolysis of all but the very smallest samples of II produced final pressures at least ten times this value.

Photolysis efficiency was greatest when the sample was placed close to the photolysis flash, so that the starting material subtended a large angle. Compound II photolyzed very efficiently in fused silica; when samples were small, yields of N_2 and CO_2 indicated that as much as 80–90% of the starting material may undergo reaction. Even in Pyrex, for II efficiencies were as high as 35–40%. Compound IV, in contrast, was not significantly affected by flashing unless it was in a silica tube, and even then only about 10–20% of the material reacted under photolysis, even in the most efficient reactions. It was difficult to obtain thin uniform films of IV. After photolyses, much of the unchanged starting material could be recovered.

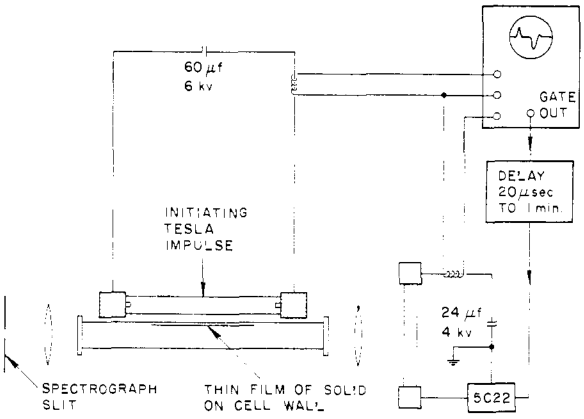

Fig. 1.—Schematic diagram of apparatus.

An oscillographic record was made for each photolysis, in which the delay time was displayed as the distance between two sharp peaks.

Spectra were taken on a variety of plates: Eastman 103-0, and Ilford HPS and Zenith, for most of the work; Ilford Q-2 and Q-3 for the far ultraviolet, and for infrared work, Eastman I-N and ammonia-sensitized I-Z plates. Plate calibration was done with a seven-step calibrated neutral density wedge. Extinction coefficients cannot be derived from the method described here because the sample distributions and concentrations and, therefore, the effective optical path lengths $l \times c$ are not known. We can, however, assume that photolysis is essentially complete for the reactive species II; by using a spectrum which shows that the sample is uniformly distributed throughout the tube, we can estimate a lower limit of the extinction coefficients at any wave length. Further, we can compare the shape of the extinction curve for II with that of IV to examine the similarity of the transient absorptions from the two different starting materials. We cannot, however, make a meaningful comparison on the basis of the observed values of absorbance themselves.

Photolysis of relatively large samples (0.1–0.2 millimole) of benzene diazonium-2-carboxylate produced a cloud of deep yellow material, which settled slowly onto the walls of the sample tube. Most of the solid was not soluble in ether, and appeared to consist of polymeric material, perhaps with some unchanged starting material. The yellow ether extracts from several large-sample photolyses were combined and evaporated to 26 mg. of deep yellow oil. Chromatography was carried out on ordinary alumina, with a solvent of 2:1 petroleum ether (30–60°)-benzene. The eluent furnished 4.8 mg. of biphenylene, m.p. 112–113° (reported[12] 110–111°), and 1.3 mg. of triphenylene, m.p. 198–199° (reported[13] 199°), each of which exhibited an ultraviolet spectrum in ethanol which was virtually identical with that reported previously.[12,14] A considerable quantity of the volatile biphenylene was lost in isolation, so that the ratio of these two products favors biphenylene more than the above figures indicate. Later work[15] has shown that biphenylene can be produced by this technique in yields as

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(11) D. A. Ramsay, *J. Chem. Phys.*, **20**, 1920 (1952).

(12) W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

(13) C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

(14) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 445.

(15) R. M. Stiles and U. Burckhardt, unpublished.

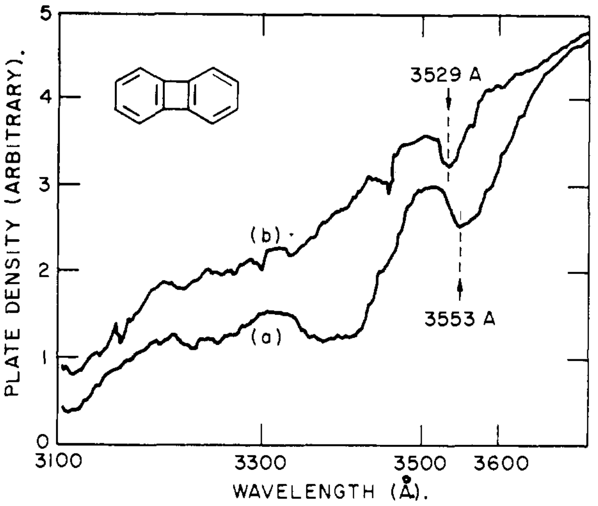

Fig. 2.—Microdensitometer tracings showing shift of long wave length bands of biphenylene with time: (A) 1 millisecond after photolysis of 20 micromoles of benzenediazonium-2-carboxylate; (B) same sample ~2 minutes after photolysis.

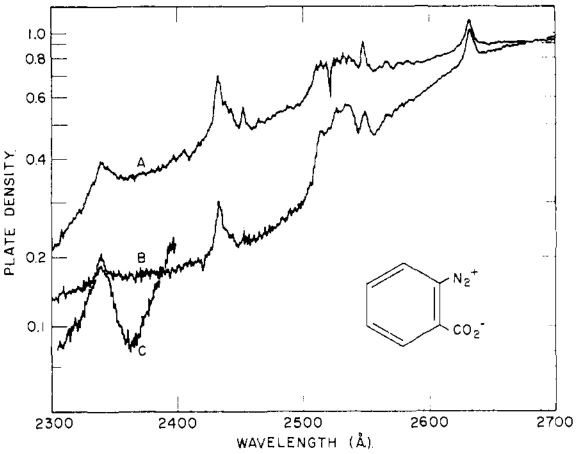

Fig. 3.—Microdensitometer tracings showing absorption by gaseous products from photolysis of benzenediazonium-2-carboxylate: (A) comparison (blank) spectrum for B, taken through neutral filter of optical density 0.592, slit 0.17 mm.; (B) 63 microseconds after photolysis of 1 micromole of sample, same slit, no filter; (C) biphenylene absorption several minutes after photolysis of 4 micromole sample, slit ~0.035 mm. All three were taken on 103-0 plates.

high as 35% of the theoretical value. Some starting material can also be recovered.

III. Results

A. Benzenediazonium-2-carboxylate.—As the preceding paragraph described, chromatography of the products of flash photolysis of benzenediazonium-2-carboxylate (II) has shown that biphenylene and triphenylene are produced in addition to CO_2 and N_2.[10,15] When large samples (0.1 millimole or more) are photolyzed, the absorption spectra of gaseous biphenylene and triphenylene are both quite intense; the former always predominated in the experiments described here. Photolyses of small samples, 0.3 to 5 micromoles, show only biphenylene and no triphenylene at times greater than about 1 millisecond after photolysis. The intense biphenylene absorption in the 2400 Å. region is always present, but the long-wave bands, the strongest of which is at 3543 Å., are not easily observed unless at least 2 micromoles of starting material are used. At times between 200 and 1000 microseconds after photolysis, the biphenylene spectrum is broader, seems weaker and is accompanied by the transient continuous absorption previously attributed to benzyne.[10] The biphenylene absorption at short wave lengths cannot be separated from this broad absorption; the long-wave biphenylene bands do appear clearly, however. These long-wave bands give very clear evidence that the biphenylene is formed with excess vibrational energy. For example, the strongest band of the long-wave group has λ_{max} at 3587 Å. one millisecond after photolysis and is rather broad. The same band of biphenylene in thermal equilibrium at 20° is considerably narrower, and has its maximum at 3543 Å., a shift of almost 350 $cm.^{-1}$ to the violet. Figure 2 shows microdensitometer tracings of these bands.

Spectra taken at short times, 20–80 μsec. after photolysis, show strong absorption which does not correspond to the known biphenylene spectrum. The extinction rises slowly from the 2700 Å. region (even the 3000 Å. region when large samples are used), and reaches a broad, flat maximum at about 2420 ± 30 Å. The position of the maximum was previously estimated at about 2400 Å.[10]; more precise densitometry has led to the revised value. Absorption rises again just below 2300 and continues to increase out to the 2000 Å. limit of the spectrograph. Tracings taken from typical spectra and comparison are shown in Fig. 3. An extinction curve based on these spectra is shown and discussed in the final section of this paper. From just the appearance of the short-time spectra (30–60 microseconds) of gaseous products from II, it is impossible to determine whether biphenylene is present, since the transient continuum extends through the 2390 Å. region where the strong, broad biphenylene absorption occurs.

Also present at short times after photolysis are absorption lines of atomic silicon. These lines, easily identifiable by coincidence with lines of the spectral flash, arise from ground-state atoms, and are definitely associated with the photolysis. They are not present when an empty tube is subjected to a flash. Successful attempts were made to eliminate this absorption by depositing the solid to be photolyzed on a Mylar or aluminum tray inserted in the sample tube. The continuous absorption reappeared but the silicon lines were absent. Efficiency of photolysis under these conditions was low and results were erratic, perhaps because the solid did not form a smooth thin film.

The atomic silicon may be produced either by a reaction between starting material or benzyne with the tube, or by the impacts of energetic molecules. Since the decomposition of compound II is quite violent and presumably quite exothermic, the latter seems somewhat more likely. In fact, it is quite reasonable that the process by which the decomposition of II occurs is not a true photolysis, but a photolytically-initiated detonation.

The continuous absorption did not reach its full intensity instantaneously after photolysis. This was more apparent when Mylar or aluminum was used as a support for the precursor than when the material was deposited directly on the tube wall. At times of about 40–60 microseconds, the intensity seemed to be fully developed. Figure 5 shows extinction curves based on two different delay times for samples deposited on the silica wall.

The finite time required for the intensity to develop is due at least partly to the finite rate of diffusion of the absorber away from the tube walls. This can be seen as a non-uniform distribution of absorber at very short times, about 20 microseconds after photolysis. The effect is much more pronounced when inert gases are present (see below). We were unable to determine whether there were other effects due specifically to the different surfaces.

Small traces of benzene are detectable in spectra taken after relatively long delays, greater than about 200 microseconds.

A series of photolyses were carried out in which a foreign gas was present in the sample tube. Some of these were done to study the possibility of vibrational relaxation or stabilization of gaseous benzyne; others were performed to try to observe true gas-phase chemical reactions of benzyne. Substances in the former class include argon, CO_2, H_2, BF_3 and diethyl ether vapor. Carbon monoxide may be placed in this class also. Partial pressures of these substances ranged from 2 to 30 cm. With none of them is there any spectroscopically detectable chemical effect, nor is there any significant change in the shape of the absorption curve. The only noticeable effect is a simple result of the lower diffusion rate of the absorbing species when the total pressure is increased. Owing to the optical arrangement, a concentration gradient across the sample cell gives rise to non-uniform illumination of the spectrograph slit. Spectra taken with various delays in effect show the absorber traveling across the sample tube.

B. Reaction of Benzenediazonium-2-carboxylate with Butadiene.—One reaction we have observed involves the flash-photolysis product from II and gaseous butadiene. The reaction can be observed when butadiene is added to the sample cell, in a large molar ratio to the diazonium salt, *ca.* 50:1. Absorption bands at 2694 and 2753 Å. are found 30 seconds after photolysis. These seem to coincide with the bands reported for the solution spectrum[16] of 1,4-dihydronaphthalene, the product expected from a Diels–Alder reaction between benzyne and butadiene. Biphenylene is still the major product, but the additional bands are clearly marked. Vapor chromatography also supports the identification of the adduct. Retention times on two columns were indistinguishable from 1,4-dihydronaphthalene. The two columns were (a) 61 cm. of silicone rubber with a programmed temperature and helium carrier, and (b) 91 cm. of silicone rubber on Chromosorb, operated isothermally at 130 and 145°, with argon as the carrier.

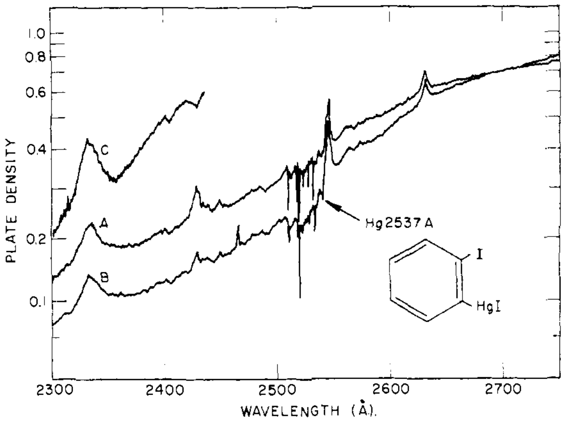

Fig. 4.—Microdensitometer tracings showing absorption by gaseous products from photolysis of *o*-iodophenylmercuric iodide: (A) comparison (blank) spectrum for B, slit 0.02 mm.; (B) 44 microseconds after photolysis of 0.75-micromole sample, same slit, Zenith plate; (C) biphenylene absorption several minutes after photolysis of ~20 micromoles of sample in the presence of H_2 at $p = 2$ cm., slit ~0.02 mm., 103-0 plate. The heavy arrow indicates absorption at 2537 Å. due to atomic mercury.

C. *o*-Iodophenylmercuric Iodide and Di-*o*-iodophenylmercury.—Samples of *o*-iodophenylmercuric iodide and di-*o*-iodophenylmercury were very kindly supplied by Professor G. Wittig. Both of these compounds are photolyzed much less readily than is benzenediazonium-2-carboxylate, as we pointed out previously. Moreover, the variety of possible final products is much greater; instead of inert N_2 and CO_2 molecules, photolytic decomposition can produce a variety of iodine and mercury-containing species, in addition to the desired hydrocarbons.

Photolysis of IV yields mercury, HI, HgI_2 and Hg_2I_2 among the final products. The first of these was detected spectroscopically and visually, and the other three, chemically. Under ordinary circumstances, biphenylene is not a significant product. Very small traces might be responsible for a possible very weak opacity in some spectra, but this apparent opacity is within the spectral noise level and must only be considered suggestive at best. No iodobenzene or *o*-diiodobenzene was detected. No specific attempt was made to detect diiodobiphenyl or 9,10-dimercura-anthracene. Free atomic mercury is detectable at short times, at a partial pressure considerably above its equilibrium value, according to the intensity of the absorption line at 2537 Å.

Short-time-delay spectra show transient continuous absorption very much like that found from photolysis of II. Figure 4 shows a microdensitometer record of this absorption, together with a comparison. Free atomic mercury is clearly present. The total intensity of the transient continuum is much lower for IV than for II, with samples of the same size; this is consistent with the observation that one can recover large amounts of unreacted IV after photolysis. The extinction curve, shown in the next section, has a minimum in the 2390 Å. region where biphenylene absorbs most strongly.

Traces of benzene can be detected in spectra taken 200 μsec. or more after photolysis. The intensity of the benzene absorption is slightly greater

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(16) W. Hückel, E. Vevera and U. Wörffel, *Chem. Ber.*, **90**, 901 (1957).

from IV than from II. As in the case of photolysis of II, the quantity of benzene formed seems to be unaffected by the presence of hydrogen gas. Possibly the benzene is produced by abstraction of hydrogen atoms from starting material (or, less likely, from the transient intermediate).

When hydrogen is present, biphenylene can be detected in spectra taken after photolysis, just as in the photolysis of II. The significant portion of a typical spectrum is shown in Fig. 4. Iodine, an iodine compound, possibly mercury or a mercury compound or perhaps all of these, seem to be able to attack the transient intermediate faster than the intermediate reacts to give biphenylene. Hydrogen somehow leads to quenching of this fast reaction, at least in part, so the biphenylene-producing reaction can occur.

Photolysis of di-*o*-iodophenylmercury in an evacuated tube produced essentially the same results as did IV: the usual transient continuum and free mercury at short times, but no biphenylene at longer times. Extensive studies of photolysis of this compound were not pursued.

There is no reason to assume or require that the transient species were produced by a true, simple photolysis of IV. It is certainly as reasonable that the photons were absorbed and degraded, and that the transient gaseous species were the result of a decomposition which was essentially thermal in nature. Flash-heating is a well-established technique for producing short-lived gaseous molecules, and may be involved here.[17]

IV. Conclusions and Discussion

The final products from photolysis of benzenediazonium-2-carboxylate, N_2, CO_2, biphenylene and triphenylene suggest that benzyne is formed as a result of the photolysis. The appearance of gaseous biphenylene at concentrations greater than the equilibrium value very soon after photolysis indicates that it is formed in the gas phase. The transient spectrum in the 2430 Å. region, which disappears as the biphenylene spectrum appears, may, according to this evidence, be due to excited biphenylene, some substituted phenyl radical or ion, or to benzyne itself.

Since flash photolysis of *o*-iodophenylmercuric iodide can give biphenylene, free mercury and what appears to be the same transient continuum as that from the diazonium salt, we presume that the mercury compound produces benzyne, as postulated by Wittig and Ebel for the steady photolysis of solutions.[9] The similarity of shapes and lifetimes of the continuous absorptions from II and IV leads us to believe that they arise from the same species. The general appearance of the broad continuous absorption and the absence, at short times, of absorption in the 3500 Å. region, leads us to believe that the transient absorber is not biphenylene in its ground electronic state.

Scattering by particles of precursor might be suggested as a possible cause of the opacity. However the presence of the maximum in the extinction curve and the shape of the curve itself would require both precursors to produce rather fine dusts with a narrow range of sizes; if the index of refraction of the precursor were 1.45, the particle sizes would be about 1700 ± ~150 Å. Even with a varying refractive index, it is virtually impossible to account for the absorption maximum in terms of scattering by a more realistic dust. Therefore, only excited biphenylene and benzyne remain as reasonable possible assignments.

Finally because, aside from simple dimerization, a reaction is found which involves only a single aromatic ring in the product, we infer that benzyne is present in significant concentration in the gas phase. We conclude further that in all probability the transient spectrum is due to a single-ring species and not to an excited state of biphenylene and is, therefore, probably the absorption spectrum of benzyne.

The possibility that biphenylene is the absorber might still be held as one remaining alternative. It is conceivable that biphenylene, when it is formed, has so much vibrational excitation that the entire appearance of the spectrum is drastically changed, and that the weak bands are so spread that they are essentially undetectable. Such a thing is known to happen in the shock-heating of benzene, for example.[18] We would then have to suppose that such highly excited biphenylene is largely removed by iodine, mercury or both, to account for the results obtained from compound IV.

The vapor spectrum of biphenylene has been examined at temperatures up to 125°. Some vibrational broadening is observed, but the short-wave length absorption band remains an order of magnitude narrower than the region spanned by the diffuse absorption. The steep edge of the band moves from about 2390 Å. to about 2415 Å. with the 30% change in absolute temperature, as one might expect for such a change, if the upper state potential surface did not have any drastic curvature. The long-wave length bands were very clearly detectable in the high temperature spectra. Biphenylene was also subjected to flash photolysis, in two ways. Samples of II and IV were rephotolyzed shortly after the initial photolysis and, except for the additional decomposition of some of the remaining IV, no new or different spectra could be found. Pure biphenylene was also photolyzed with a high-efficiency helical flash lamp, and again no sign of the broad transient spectrum or of any other new spectrum was found. These experiments support, but certainly cannot prove, the working assumption that excited biphenylene is not responsible for the transient absorption. They do rule out biphenylene having a moderate thermal energy above room temperature, and they also eliminate the possibility that biphenylene is formed very rapidly and then is itself affected either by the remaining light of the photolysis flash or by the spectral flash. The experiments do not eliminate the following three possibilities. All three of these we consider rather unlikely. One might assume either that biphenylene carries the bulk of the evolved energy in a very few degrees of

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[17] L. S. Nelson and J. L. Lundberg, *J. Phys. Chem.*, **63**, 433 (1959); L. S. Nelson and N. A. Kuebler, *J. Chem. Phys.*, **33**, 610 (1960).

[18] C. E. Campbell and I. Johnson, *ibid.*, **27**, 316 (1957).

freedom for several hundred collisions, or that the upper electronic state of the short-wave length system has a sharp drop in its potential energy surface relatively far from the equilibrium configuration of the ground electronic state. The third possibility is the chance that the transient species is a biphenylene triplet (diphenyl diradical). Except for the appearance of the 1,4-dihydronaphthalene and benzene, and the absence of biphenylene as a normal product from IV, there is no strong experimental evidence to exclude this species. One argument might be raised against it, namely, the problem of spin conservation. If benzyne reacts as a singlet, in its ground state, then it would be reasonably difficult to produce a triplet biphenylene in a dimerization reaction. It would be necessary to require that a large amount of triplet benzyne were available for reaction with itself or with singlet benzyne, in order to form the required high concentration of diradical.

It should be mentioned at this point that an emission spectrum has been observed by Schüler and Lutz[19] which they attribute to benzyne. The "W-Spectrum," a continuum between 3400 and 4400 Å., is observed in discharges through a flowing mixture of a small amount of helium together with any of a number of organic substances, including the halobenzenes, biphenyl, phenylacetylene and benzene itself. This spectrum appears when the discharge tube is heated to 200–300°. To compare this emission continuum with the absorption continuum described in the foregoing sections is at best to tread a precarious path. We can say only that it is consistent to assign both the emission and the absorption to benzyne on the following grounds. Benzyne almost certainly enjoys a singlet ground state.[6,7] Then both of the "odd" electrons are in an orbital whose density maximum is in the molecular plane, and which acts as a bonding orbital between the two hydrogen-less carbon atoms. This orbital is much like a π-orbital of ethylene, but probably higher in energy.

Some preliminary Hückel-model estimates have been made to estimate the order and magnitudes of the orbital separations.[20] These were based on application of the "magic formula" variation of the off-diagonal matrix elements,[21] with $\beta = 20$ kcal./mole for the benzenoid system and $\beta = 20 \times s'/s$ for the in-plane orbitals (s = overlap integral), respectively, and from atomic valence-state ionization potentials.[22] These very crude results suggest that the in-plane orbital analogous to the bonding π-orbital of ethylene has an energy a little lower than the highest filled benzenoid π-orbital. The ethylene-like anti-bonding orbital is expected to lie somewhat closer to the filled bonding orbital than it does in ethylene. One is led to suppose tentatively that the observed transient absorption is due to the transfer of an electron from the bonding in-plane orbital to the corresponding anti-bonding orbital. The other reasonable possibility would assign the transition to the transfer of an electron from a benzenoid π-orbital to the unfilled ethylenic orbital. This transition probably would fall at much longer wave lengths, however, possibly in the photographic infrared region. In either case a new anti-bonding electron is introduced in the region of the "triple bond." If a benzenoid π-orbital is involved, the electron may be either bonding or non-bonding initially; more detailed calculations will be required to determine which it is. (Perhaps both kinds are involved.) If only the in-plane orbitals are involved, then the electron is bonding, initially. Both cases suggest that the excited state will have an equilibrium geometry which differs considerably from that of the ground state. Hence one expects a broad and diffuse absorption spectrum. If this is the case, emission from the upper state is expected to be continuous also, and to lie at considerably longer wave lengths than the absorption. We therefore feel that the spectrum reported by Schüler and Lutz and the absorption spectrum we report may be consistently assigned to the same species, and to the same transition.

Spectral investigations were carried to wave lengths as great as 12,000 Å. in a search for the "$\pi \rightarrow n^*$" transition. Samples up to about 10 micromoles give no detectable absorption, other than the long-wave tail of the continuum described above. When samples of 50 micromoles were used, the sample tube appeared nearly opaque to the spectral flash for time delays of 30–60 microseconds. Samples of 12–20 micromoles did show some opacity in the region between 9000 and 4000 Å. However, no banded structure has been detected, nor has any maximum been found at this time. It is, therefore, impossible to say at the present time whether the opacity is due to scattering, absorption from the short-wave length transition or absorption from a different, low-energy transition. Further investigations of the long-wave length region are planned, based on the use of a multiple traversal sample cell.

Because of the sample sizes used, it is possible to set a very rough upper limit on the extinction coefficient for a low-energy transition. This limit is $\epsilon < 100$. A low extinction is to be expected, unfortunately, because, first, the transition has its electric vector perpendicular to the ring, like an $n \rightarrow \pi^*$-transition of pyridine, so that the dipole of the transition is small. Second, if the interior angle at the "triple bonded" carbon atoms is greater than 120°, the amount of s-character of the excited orbital will be less than the 33% of an sp^2-orbital, and it is this s-character which would give most of the allowed character to the transition. Third, the transition is presumably much broader than an $n \rightarrow \pi^*$ transition, since the upper state of the benzyne transition has an extra anti-bonding electron which will cause the geometry of the molecule to change. These three reasons suggest that the transition may be rather difficult to locate unambiguously.

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(22) I. J. Goldfarb and H. H. Jaffé, *J. Chem. Phys.*, **30**, 1622 (1959).

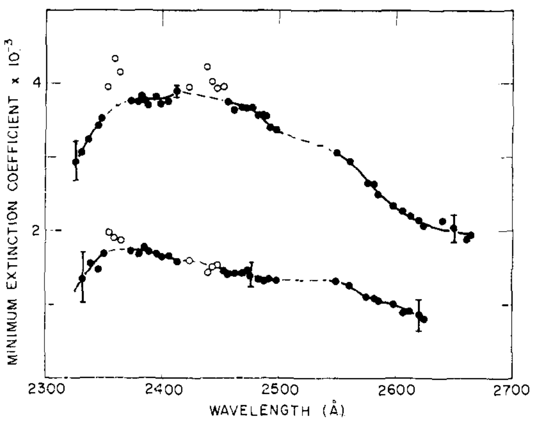

Fig. 5.—Relative extinction curve for transient absorption from typical photolysis of benzenediazonium-2-carboxylate. Points are those for which photometric measurements were made. Open circles and dotted portions of the curve indicate regions of severe interference by silicon. The ordinate would give the extinction coefficient, were the assumptions described in the text actually fulfilled; it in fact represents a lower limit on ε. Data: 1 micromole of sample, slit 0.17 mm., 103-0 plate; upper curve, 63 microseconds after photolysis; lower curve, 33 microseconds after photolysis.

We conclude with a presentation of relative extinction curves obtained from photolyses of benzenediazonium-2-carboxylate and *o*-iodophenylmercuric iodide. Figure 5 is a plot of the extinction derived from photolysis of the diazonium salt, based on a typical plate. The ordinate scale would represent the extinction coefficient if the sample were entirely photolyzed, if only a single absorbing species were present, if one absorbing molecule were produced per molecule of starting material, and if the absorbers were all present in the gas phase simultaneously. The diazonium salt appears to satisfy the first condition reasonably well; the second apparently is satisfied at short times and the third is almost equivalent to saying that the transient species is benzyne. Whether the fourth condition is satisfied cannot be answered on the basis of existing information. The instantaneous concentration of the transient species is not known. Therefore, the values of the extinction coefficient in Fig. 5 may be taken as lower limits to the true extinction coefficient.

A similar curve is given in Fig. 6 for the transient absorber produced from *o*-iodophenylmercuric iodide. The low numerical values on the ordinate simply reflect the exceeding inefficiency with which this compound is flash-photolyzed.

Except for the region 2380–2400 Å., the upper curve of Fig. 5 and the curve of Fig. 6 are indistinguishable, within experimental error. By way of comparison, the two curves of Fig. 5 differ more from each other than do the two 70-microsecond spectra. It is very important to note that the one region in which the curves of Fig. 5 do differ from that of Fig. 6 is the region of very intense biphenylene absorption. The obvious inference to be drawn from the spectra and from the products cited earlier is simply that some biphenylene is formed very shortly after photolysis, and that its spectrum is sufficiently broad that it merges into the broader diffuse absorption at longer wave lengths.

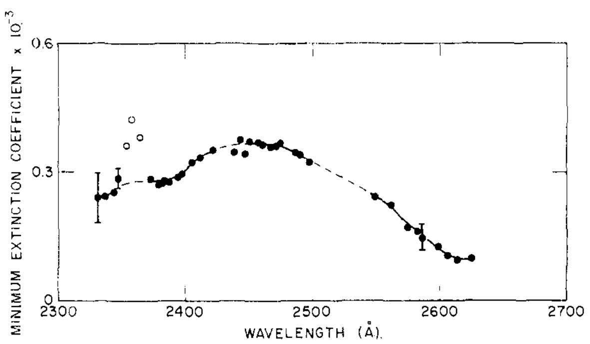

Fig. 6.—Relative extinction curve based on typical spectrum from photolysis of *o*-iodophenylmercuric iodide. Points are those for which photometric measurements were made. Open circles and dotted portions of curve indicate regions of severe silicon interference. Numbers on the ordinate scale represent a lower limit on the extinction coefficient for this particular spectrum; they can be taken to represent an arbitrary scale, in view of the values shown in Fig. 5. Data: 5-micromole sample, 70 microseconds after photolysis, slit ~0.03 mm., 103-0 plate.

The errors inherent in the extinction values are relatively large, and appear as a lack of reproducibility from plate to plate. This in turn probably is due to irreproducibility of the initial photolytic decomposition. It is quite possible that the decomposition of the diazonium salt proceeds through a photolytically-initiated detonation, and may be a very sensitive function of the way the sample is distributed on the cell walls. Between 3000 and 2400 Å., the relative error in Fig. 5 is probably of the order of 15%. Beyond 2400 Å., it starts to increase and is perhaps as high as 50% in the 2300 Å. region. The curve of Fig. 6 has a larger uncertainty associated with it, of the order of 25% out to 2400 Å. and again may be off by as much as 50% in the 2300 Å. region. From the curve of Fig. 5, we estimate the oscillator strength of the transition to be of the order of magnitude of 0.1–0.2.

It is not at all surprising that spectra taken at different times, but less than about one hundred microseconds after photolysis, have somewhat differently-shaped extinction curves. The total pressures after photolysis are only a few mm. Therefore the gaseous molecules may experience as many as three or four thousand collisions, and will undergo considerably fewer than a thousand, if the sample is small and the spectrum is taken rapidly. This number is comparable to the very shortest collision numbers required for vibrational relaxation.[23] As a result, one must expect that the distribution of molecules among vibrational states will change significantly during the interval between 10 and 100 microseconds after photolysis. Any spectra recorded during this time will show corresponding variations. Specifically, one expects that broad curves will grow narrower and maxima will shift to shorter wave lengths, just as the bi-

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[23] See, for example, the results summarized by D. F. Hornig, *J. Phys. Chem.*, **61**, 856 (1957).

phenylene curves of Fig. 2 and the transient curves of Fig. 5 do.

Despite the large uncertainties in the curves, their time-variation and especially their shapes lead us to assume that the two absorptions are due to the same species. In all, the weight of the evidence supports the assignment of this absorption to benzyne.

V. Acknowledgments.—We would like to thank Professor Georg Wittig for suggesting that *o*-iodophenylmercuric iodide and di-*o*-iodophenylmercury be studied by flash photolysis, and for supplying us with samples of these compounds. We would also like to thank Mr. Roy Miller for supplying the benzenediazonium-2-carboxylate and Mr. Wayne Warren for his part in the construction of the apparatus. We are grateful to the Bridgeport Brass Co. for the use of their recording microdensitometer. Finally, we would like to express our gratitude to the U. S. Air Force Office of Scientific Research for the grant under which this work was performed.

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π-Complex Interactions between Trinitrofluorenone and Polycyclic Aromatic Hydrocarbons[1]

BY ARTHUR R. LEPLEY

RECEIVED APRIL 30, 1962

The charge-transfer spectra of the π-complexes formed by trinitrofluorenone with a number of polycyclic hydrocarbons have been measured. The application of molecular orbital theory to π-complexes is supported by these data. A relationship between charge-transfer bands and donor π–π^*-transitions is proposed and used in evaluation of molecular orbital parameters for fluoranthene and fluorene analogs of the polycyclic aromatics.

A simple molecular orbital treatment has been developed[2,3] which describes the weak attractions between aromatic compounds and such materials as trinitrobenzene, tetracyanoethylene, bromoanil or tetrachlorophthalic anhydride. The forces between these molecules observed through charge-transfer transitions were considered to be intramolecular orbital interactions. Molecular compounds of this type, π-complexes, have been observed in the solid state and in solution.

In general, π-complex formation results in little perturbation of the molecular orbital energy levels of the donor molecule (A) or of the acceptor (B). The weakness of the perturbational influence has been demonstrated by the invariance of transition energies for the principal component electronic energy absorptions.[4] The solid state absorption spectrum is composed of the bands characteristic of pure A and B as well as charge-transfer bands.

The energy, ΔE_{ij}, for an electronic transition is given in simple molecular orbital theory[5,6] by the difference in orbital energies, *m* (eq. 1)

$$\Delta E_{ij} = m_j - m_i \qquad (1)$$

where the subscripts j and i denote the *j*th and *i*th orbitals, respectively. The energy, E_π for the new charge-transfer band which occurs on excitation of the π-complex similarly requires the transfer from the *i*th orbital of the donor to the *j*th orbital of the acceptor

$$E_\pi = B_j - A_i \qquad (2)$$

where A_i and B_j are the respective orbital energies for the donor A and the acceptor B. The energy of a filled orbital for polycyclic aromatics, as given by the Hückel molecular orbital treatment, is $\alpha + x_i\beta$. Here α is the coulomb integral for carbon, x_i is a quantity calculated theoretically for the *i*th orbital, and β is the carbon–carbon resonance integral. When a value of x_i corresponding to the highest filled orbital of a donor hydrocarbon is used, the transition energy for the first π-complex charge-transfer band should be

$$E_\pi = B_j - \alpha - x_i\beta \qquad (3)$$

If the same acceptor is used with a number of donors, the energy of the lowest unoccupied acceptor orbital will be constant. Under these conditions a linear relationship should exist between the theoretical quantity x_i and the transition energy E_π. The values of β and $B_j - \alpha$ will then be given, respectively, by the slope and the intercept x_i times β at $E_\pi = 0$ of this line.

Internal transitions have been thoroughly treated and summarized.[7,8] These transitions take place between filled and unfilled orbitals in a single molecule. When the donor hydrocarbon A is considered, the transition energy E_A should be

$$E_A = A_j - A_i \qquad (4)$$

where A_i and A_j are, respectively, filled and unfilled orbitals of molecule A. If the donor is a polycyclic aromatic hydrocarbon, the x_i for unfilled orbitals have the same values but are opposite in sign to those of the filled orbitals. The energy of the lowest unfilled orbital is then

$$A_j = \alpha - x_i\beta \qquad (5)$$

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(1) This work was supported by a grant from the Research Foundation of the State University of New York.

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