

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Mercury Photosensitized Reactions Involving Benzene and Hydrogen

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Bates and Taylor¹ irradiated benzene vapor in a flow system with a mercury vapor lamp, and found the decomposition to be negligible. After admitting mercury vapor, very small amounts of hydrogen and methane were detected. "A heavy tarry residue is deposited on the reaction vessel, and a strong odor of diphenyl is present."

Bonhoeffer and Harteck² combined a stream of atomic hydrogen at 1 mm. pressure with a stream of benzene vapor at about one-sixth that pressure. A green "flame" was noted in the reaction zone. In a typical experiment 2.20 g. of benzene was used, of which 1.80 g. was recovered, apparently unchanged, in a trap cooled by carbon dioxide snow in ether. The gases not arrested at -78° were further investigated in subsequent experiments. By condensation in liquid air boiling under diminished pressure, followed by fractional evaporation at -115° and at -78° , methane was identified, and indications were obtained of other hydrocarbons, presumably ethane or ethylene. Obviously hydrogen atoms (in large excess) had disrupted the benzene rings.

Krassina³ exposed benzene vapor to radiation from an aluminum spark, and showed that the effective wave length range must be 1850 to 2000 Å., since zinc radiation (2030 to 2150 Å.) was much less effective, and cadmium radiation (2150 to 2300 Å.) was without effect. Disruption of the benzene ring was considered improbable, and the primary act $C_6H_6 + h\nu \rightarrow C_6H_5 + H$ was adopted as a working hypothesis. No test for phenyl radicals could be devised, but hydrogen atoms were detected by their action on tungsten oxide and on copper sulfate. In addition, a deposit upon the walls was supposed to be diphenyl.

Prileshajeva⁴ assumed the same primary act as Krassina. Apparently she had misunderstood the findings of Bonhoeffer and Harteck, since she states that "atomic hydrogen is known to behave inertly with respect to benzene vapor." She assumed that the hydrogen atoms must have combined exclusively with each other while phenyl radicals gave rise to unidentified products.

Under the conditions of one experiment, 1.45×10^{12} hydrogen molecules were produced per second by a zinc spark and 7.8×10^{12} molecules per second by an aluminum spark.

Our interest in these reactions arose from previous experiments, starting with the mercury sensitized decomposition of carbon dioxide⁵ which was effected only through resonance radiation, 1849 Å., and not through that of wave length 2537 Å. Unsensitized photolysis, in light of wave length less than 2000 Å., occurred in absence of mercury. Subsequently, using the same apparatus and technique, it was shown that toluene, *p*-xylene, phenol, ethane and monochlorobenzene all decomposed rapidly in presence of mercury vapor excited by resonance radiation of wave length 2537 Å. even after that of wave length 1849 Å. had been filtered out. Naphthalene vapor, with mercury, reacted very slowly in both unfiltered and filtered radiation.

Our capillary resonance lamp emitted about 2% of its total radiation⁵ with wave lengths less than 2000 Å. This could be intercepted by a filter of 0.005 *M* sodium nitrate having an effective thickness of about 12 mm. Using this filter, benzene vapor plus mercury evolved a negligible volume of gases not condensed at -78° , whereas very small, but still measurable, amounts of such gases were produced in the absence of a filter. To test further this outcome, the total pressure of benzene vapor, with products, was followed in three experiments graphed in Fig. 1. In the first part of Experiment A, and C, the filter transmitted completely resonance radiation of wave length 2537 Å., but practically no photolysis occurred, as shown by the nearly horizontal course of the curves. Upon removing the filter, at the times indicated by the arrows, a rapid reaction set in, which can have been due only to the relatively small amount of radiation of wave length less than 2000 Å. Experiment B was conducted entirely in unfiltered radiation, but mercury vapor had been trapped out, pretty completely, at -8° . The slope of the curve shows that mercury is not essential to the reaction.

Carefully dried phenol vapor, with mercury, was next subjected to action of filtered radiation, 50 to 75° . Ten experiments were performed. The pressure fell rapidly at first, passed through a minimum in about twenty minutes, and within twelve hours increased beyond the original value. Several experiments were interrupted after about fifteen minutes and the products investigated by physical analysis. A typical set of data follows: initial phenol 3.09 mm., final phenol 1.58 mm., phenol consumed 1.51 mm., water formed 0.28 mm., hydrogen formed 0.14 mm.

(1) Bates and Taylor, *THIS JOURNAL*, **49**, 2438 (1927).

(2) Bonhoeffer and Harteck, *Z. physik. Chem.*, **139**, 64 (1928).

(3) Krassina, *Acta Phys. U. R. S. S.*, **10**, 189 (1939).

(4) Prileshajeva, *ibid.*, **10**, 193 (1939).

(5) Cline and Forbes, *THIS JOURNAL*, **64**, 716 (1939).

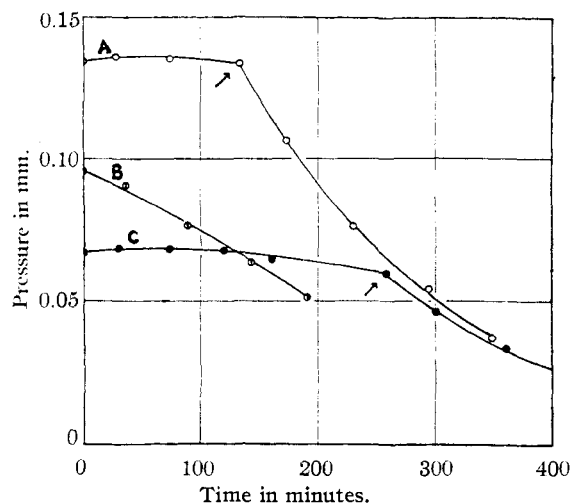


Fig. 1.—Irradiation of benzene with and without a sodium nitrate filter.

If it were assumed that two molecules of phenol gave rise to one molecule of water or one molecule of hydrogen, $p_{H_2O} + p_{H_2}$ should equal 0.75 mm. instead of 0.42 mm. But this deficiency might have resulted from addition of hydrogen atoms to aromatic rings, producing free radicals capable of forming substances of high molecular weight. To decide whether hydrogen is stable under the above conditions in presence of phenol, an additional experiment at 75° was run for twelve minutes: initial phenol 4.33 mm., initial hydrogen 2.62 mm., phenol consumed 3.64 mm., water formed 0.42 mm., hydrogen consumed 2.01 mm. The moles of water produced per mole of phenol consumed was not increased by the addition of hydrogen. Since nearly five molecules of hydrogen disappeared for each molecule of water formed from phenolic hydroxyl groups, at least nine-tenths of the hydrogen gas added must have entered the aromatic rings. Even when no hydrogen was added, similar reactions were evidently evoked by hydrogen atoms liberated from phenol. But in the case of benzene, filtered radiation of wave length 2537 Å. could not lead to such reactions in the absence of added hydrogen.

Preliminary experiments were next undertaken upon mixtures of benzene vapor and hydrogen gas nearly saturated with mercury at 50° . At the beginning of a typical experiment, $p_{C_6H_6}$ was 13.31 mm. and p_{H_2} was 10.34 mm. After 107 minutes exposure to filtered radiation, total pressure was 5.13 mm. The vapors of benzene and of condensation products were frozen out by cooling the lower part of the reaction vessel to -78° , after which p_{H_2} was only 0.06 mm. Benzene and hydrogen molecules had disappeared in the ratio 8.24/10.28 or 0.80. A white solid not readily volatilized, had condensed upon the walls. It had a strong fluorescence, and upon opening the apparatus was partially dissolved by hot benzene. Such a material would be formed from benzene by a series of photochemical reactions too complicated to be readily disentangled. Therefore the apparatus was reconstructed (Fig. 2) to isolate the earlier condensation products. Benzene-hydrogen mixtures from the three-liter reservoir R were rapidly circulated through the quartz reaction vessel Q, containing

liquid mercury. The graded seal at E, and the ground joint at G (sealed with "Varno-cement") connected this vessel with the Pyrex train. L is the resonance lamp (Braun Fluorolight) and T the trap for collection at room temperature of the initial condensation products. The oven H, insulated with 1 inch of rock wool, was maintained at about 55° . Through V, the reactants could be introduced or the system evacuated by suitable apparatus not shown in the diagram.

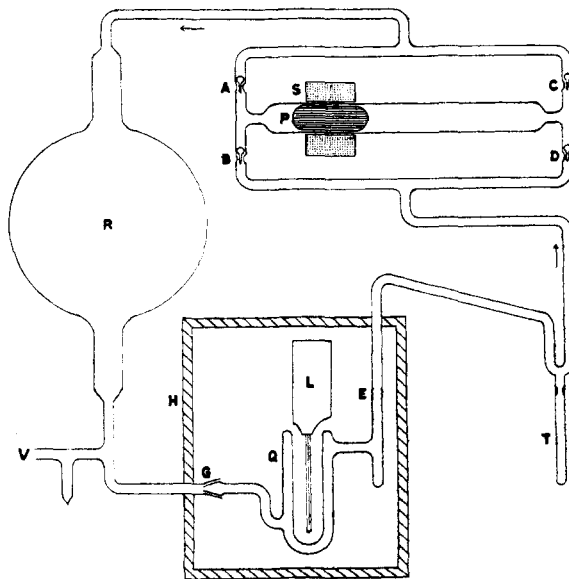


Fig. 2.—Apparatus for irradiation of circulating gaseous mixtures and collection of early photochemical products.

The double-acting circulating pump beyond the trap was similar in its fundamental principle to that of Balsbaugh, *et al.*⁶ It was found, however, that the glass piston P, packed with iron wire and sealed at both ends, could be made of 25-mm. Pyrex tubing, carefully selected to fit into the glass cylinder so closely that grinding was not necessary. The solenoid S, activated by direct current, was mounted in a carriage which was pulled back and forth along the glass cylinder in the one direction by means of a string attached over a pulley to an eccentric and in the other by a string running over a pulley and attached to a weight. The valves A, B, C, D were simply small bulbs, with tails, which were seated in constrictions in the 10 mm. tubing of which part of the pump was constructed. When the piston P moved toward the right, valves A and D opened while B and C remained closed. With motion toward the left the action of the valves was reversed, but the gases still moved in the direction of the arrows. The valves were so light that they functioned properly when the average pressure of the circulating gas was as low as 1 mm.

Several samples were prepared at 55° in this apparatus. The initial partial pressures of the reactants were close to 75 mm. each, and the mixture was exposed to unfiltered radiation for about thirty hours. In each run about 0.6 cc. of almost colorless liquid condensed in the trap T, from which it was possible to obtain a fraction of 0.3 cc. boiling at

(6) Balsbaugh, Larsen and Lyon, *Ind. Eng. Chem.*, **28**, 682 (1936).

about 200° which proved to be highly unsaturated. This was soluble in benzene, ether and absolute alcohol. It dissolved in concentrated sulfuric acid to form a deep red solution from which sulfur dioxide was slowly evolved.

The volatile fraction, containing much benzene, absorbed bromine readily, indicating the presence of unsaturated compounds. After expelling benzene from the brominated material and purifying the residue by crystallization from absolute alcohol and two sublimations, well crystallized white needles were obtained which melted 187–188°. The thermometer was calibrated in boiling aniline. Although no analysis was made, it should be noted that 1,2,4,5-tetrabromocyclohexane melts at 188⁰⁷ and that all other bromine derivatives of benzene and cyclohexane have melting points very different from this temperature. Presumably, then, a cyclohexadiene was one of the original photochemical reaction products.

The first sample of crude photochemical reaction product was washed out with xylene and the solution boiled down to 2 cc. to expel benzene and other volatile substances. The residue was refluxed with chloranil for twenty-one hours to dehydrogenate the ring.⁸ Upon cooling, a brownish-red solid, presumably crude tetrachlorohydroquinone, appeared, which was filtered off on glass wool and washed with xylene. In a separatory funnel, ether was added to the combined xylene solutions, and the mixed liquid shaken several times with 4% potassium hydroxide to remove hydroquinone and excess chloranil, then with water. Upon driving off the xylene at 100° in a vacuum, 0.2 cc. of a dark colored liquid remained, which upon cooling turned for the most part into a white solid. This was purified by two sublimations. Its melting point was 68–69°; that of pure diphenyl was 70–71°; the mixed melting point was 69–71°. All three melting points were determined in the same apparatus. It was thus proved that the most important photochemical product, under the conditions obtaining in the reaction, was a hydrogenated diphenyl.

The second sample of crude reaction product was freed from benzene by boiling (in air) and evacuating under the oil pump. To determine the degree of unsaturation, about 0.07 g. was at once further hydrogenated using Adams platinum oxide catalyst,⁹ in absolute alcohol, in a closed system of about 110 cc. total volume. The capsule containing 0.0684 g. of reactant was dropped into the alcohol by a magnetic release, but only after the catalyst had been completely hydrogenated with gaseous hydrogen. The decrease in volume, measured on a gas buret connected through a coiled 4-mm. copper tube 1.5 meters long to expedite shaking, was 33.9 cc. at 23° and 764 mm. If the average molecular weight of the reactants is about 160, then each mole has added 3.3 moles of hydrogen.

After three days of exposure to the atmosphere, a microanalysis showed 8.56% H and 80.18% C. The ratio H/C = 0.106. The remainder, 11.26%, was presumably oxygen absorbed from air.

Of the radicals capable of union to form hydrogenated diphenyls, cyclohexenyl, C₆H₉·, has one active double bond and cyclohexadienyl, C₆H₇·, has two such bonds. United, C₆H₉-C₆H₉ has two double bonds and the ratio H/C is

0.1260; C₆H₉-C₆H₇ has three double bonds, and the ratio H/C is 0.1121; C₆H₇-C₆H₇ has four double bonds, and the ratio H/C is 0.0981. As more than four reactive double bonds cannot be present, both the hydrogen uptake and the analysis of the photochemical product are plausibly expressed as 35% C₆H₉· and 65% C₆H₇· distributed among the three combinations mentioned above. This composition requires a ratio H/C of 0.108 and a hydrogen uptake of 3.3 moles. Of course, a number of isomers due to different positions of double bonds could be anticipated. All other imaginable hydrogenated diphenyls correspond either to a very different ratio H/C or to a very different hydrogen uptake, or both.

A third sample was prepared and freed from volatile substances without admission of air into the system. The trap T (Fig. 2) with the product was sealed off. After opening the trap, both the microanalysis and the measurement of hydrogen uptake were completed without delay. The percentages of H and C were 9.54 and 87.98, respectively, leaving only 2.48% to be attributed to oxygen. The ratio H/C was 0.108 in good agreement with the previous value 0.106. Evidently oxygen adds itself without eliminating hydrogen. The hydrogen absorption, 3.4 moles per mole of hydrogenated diphenyl, also agreed well with the previous value 3.3. These results, again, are consistent with an over-all content of 35% C₆H₉· and 65% C₆H₇·.

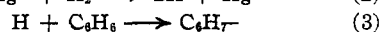
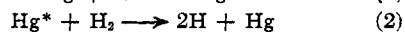
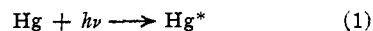
The boiling of this product, observed by the capillary method, was found to begin at 170°; the second half boiled at 233°. It was calculated that addition of 4.6% benzene by weight would have been sufficient to lower the initial boiling point of this residue to 170°. Assuming that 4.6% of benzene was present in the sample analyzed, the average ratio H/C for the hydrogenated diphenyls alone becomes 0.108 instead of 0.107 and the average hydrogen uptake becomes 3.5 instead of 3.35. The difference between measured and corrected values is within experimental error, so that the probable 5% admixture of benzene could not have vitiated the results.

The molecular weight of the product, obtained by the depression of the melting point of camphor, was found to be 151. A mixture of 5% benzene with a product of average molecular weight 160 should give an apparent molecular weight of 152.

The refractive index, *n*^{20.2D} 1.5410 (Abbe refractometer) and the density *d*²³, 0.976 (micropycnometer) fit in well on curves of refractive indices and densities of eight known hydrogenated diphenyl derivatives plotted against the hydrogen content.

The total bromine uptake was 2.2, 2.6 and 2.7 moles in successive experiments, but from the reaction products 1.0, 1.2 and 1.3 moles of hydrobromic acid were recovered. Evidently the fraction of the bromine not added to double bonds had been substituted for hydrogen atoms, or else had removed them directly as hydrobromic acid.

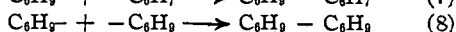
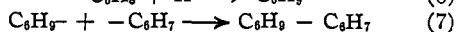
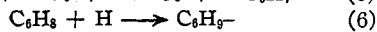
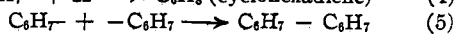
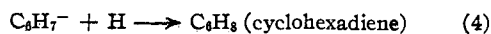
The data obtained in this investigation can all be explained in terms of the following reaction scheme



(7) Zelinsky and Gorsky, *Ber.*, **41**, 2481 (1908).

(8) Arnold and Collins, *THIS JOURNAL*, **61**, 1407 (1939).

(9) Adams, Voorhees and Shriner, "Organic Syntheses," John Wiley and Sons, Inc., Vol. VIII, p. 92, 1928.



The reaction



is inferred to be unimportant, in spite of the relatively high concentration of benzene, because analytical data and hydrogen uptake, alike, indicate that little if any phenylcyclohexadiene was present in the reaction products.

As the concentrations of reaction products (5) and (7) increase, the addition of hydrogen atoms to them, and their combination with other free radicals to form hydrocarbons of still higher molecular weight would be anticipated. The solid products deposited upon the walls of the vessel in the prolonged early experiments could be formed by reactions of this type.

We hope to investigate further the effects of changing experimental conditions, upon the relative quantities of reaction products.

In our procedure the concentration of atomic hydrogen was very much smaller in comparison with benzene concentration than in the apparatus of Bonhoeffer and Harteck.² Therefore the difference in products obtained does not necessarily involve any contradictions.

In this connection, recent investigations upon propane are of interest. Upon reaction with atomic hydrogen in relatively high concentration¹⁰ (from a Wood's tube), molecules containing smaller numbers of carbon atoms are formed. Mercury sensitization¹¹ with relatively low concentration of atomic hydrogen, produces mainly aliphatic hydrocarbons of higher molecular weight. Moore and Taylor¹² by mercury photosensitized hydrogenation of olefins, C_nH_{2n} , obtained mainly $\text{C}_{2n}\text{H}_{4n+2}$ with smaller quantities of $\text{C}_n\text{H}_{2n+2}$.

We are indebted to Miss Eleanor Werble of

(10) Steacie and Parlee, *Trans. Faraday Soc.*, **35**, 854 (1939).

(11) Steacie and Dewar, *J. Chem. Phys.*, **8**, 571 (1940).

(12) Moore and Taylor, *ibid.*, **8**, 504 (1940).

Converse Laboratory for the microanalyses reported above.

Summary

Benzene vapor is decomposed by mercury vapor excited by resonance radiation of wave length 1849 Å., or by unsensitized radiation of wave length less than 2000 Å. Like carbon dioxide benzene vapor is not decomposed by mercury excited by resonance radiation of wave length 2537 Å.

Phenol vapor is decomposed by mercury vapor excited by resonance radiation of wave length 2537 Å. A more rapid reaction occurs after hydrogen is introduced. Little water is formed, and most of the hydrogen seems to be added to aromatic rings.

Mixtures of benzene vapor and hydrogen, both at 75 mm., and saturated with mercury vapor at 55° were exposed to resonance radiation, mostly of wave length 2537 Å., in a circulating flow system which condensed out the earlier reaction products as liquids without opportunity for further irradiation.

A relatively volatile reaction product appeared to be a cyclohexadiene, since after its bromination 1,2,4,5-tetrabromocyclohexane was identified by its melting point.

The less volatile reaction products contained hydrogen and carbon in the ratio 0.107. Dehydrogenation by chloranil yielded diphenyl. Corrected for unremoved benzene, the average molecular weight was close to 160. The boiling point of the mixed products was 233°. Hydrogenated in the presence of Adams catalyst, 3.4 moles of hydrogen was taken up. These data point, quite unambiguously, to three hydrogenated diphenyls formed by combinations between the free radicals C_6H_9^- and C_6H_7^- . Measurements of refractive indices and densities were consistent with this conclusion.

A tentative reaction scheme is proposed.

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