THE FORMATION OF BENZENE IN THE RADIOCHEMICAL POLYMERIZATION OF ACETYLENE

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In view of the similarity (7) between photochemical and radiochemical reactions it was decided to make an absorption spectral analysis of acetylene polymerizing under the influence of radon. This method has already been applied to the corresponding photochemical reaction by Kato (4), Kemula and Mrazek (6), and Livingston and Schiflett (10), who detected the presence of benzene (4, 6, 10) and naphthalene (6) in the polymerizing gas in addition to the solid cuprene-like polymer reported by various authors (2, 1, 15, 9, 16). The ultra-violet absorption spectrum of benzene (3) is exceedingly distinct and well established, and its presence during the course of the reaction can easily be detected spectroscopically. To anticipate the results of our experiments, we may state that an appreciable quantity of benzene was produced. Actually it was possible to condense a volatile liquid from the acetylene–radon mixture by freezing in solid carbon dioxide plus acetone. This liquid proved to be chiefly benzene.

It is not surprising that in the earlier publications, analysis had failed to reveal the presence of benzene. Mund and Koch (14) weighed the amount of solid polymer ("cuprene") produced, after first pumping out the reaction chamber, and found that the weight of solid corresponded to the disappearance of acetylene. However, weighings were made in air some time after collection of the polymer, thereby permitting absorption of oxygen from the air[2] (5). The procedure of Lind and Bardwell (8) likewise was not designed to detect a volatile liquid.

EXPERIMENTAL

Materials

Acetylene was prepared from calcium carbide in the usual manner (11). The purifying train consisted of strong solutions of sodium hydroxide,

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[2] Kaufmann (5) mentions a pale yellow solid polymer formed from acetylene in the silent discharge. This cuprene-like polymer absorbs oxygen rapidly. Unpublished work by Lind and Schiflett (J. Am. Chem. Soc., February, 1937) indicates a similar absorption of oxygen by the radiochemical polymer.

acidified potassium chromate, and mercuric chloride, as well as tubes of solid calcium chloride and phosphorus pentoxide. The chemically purified gas was frozen in liquid air, and the permanent gases pumped off. After permitting the solid acetylene to evaporate, the process was repeated several times. Before filling the storage containers the solid was fractionated, only the middle portion being collected.

Radon was obtained from the radium chloride solution which serves this laboratory. The method of purifying the radioactive gas has been described elsewhere (12).

The benzene employed was Kahlbaum's "extra pure crystallizable free from thiophene," which was rid of permanent gases by repeating the cycle of freezing in liquid air, pumping while solid, and melting.

Spectroscopic apparatus

The cylindrical absorption tube (C) used was of ordinary glass 2 cm. x 20 cm., with circular quartz plates (2 mm. thick) sealed to each end by means of picein. A Leiss hydrogen lamp (Al electrodes; 4 mm. pressure), designated by D, constituted the source of continuous ultra-violet light. It was operated on 50-cycle A.C. current at 3200 volts and drew 0.1 ampere. The plate included below shows that no photochemical polymerization to benzene resulted from illumination during the thirty minutes exposure time required for distinct pictures. Apparently the cuprene formed in the absorption tube when radon had to be admitted did not obscure the plate.

Spectra were recorded by a Hilger E 1 quartz prism spectrograph (S) set for the region 2700–2300 A.U. Gevaert Super Chromoso # 2000 antihalo plates were employed. The wave length scale was calibrated by means of an iron arc (1.5 min. illumination). Plates were compared by visual inspection.

EXPERIMENTS AND RESULTS

The reaction took place in a cylindrical vessel (A) with a diameter of 4.9 cm. and a length of 50 cm. Container A was first sealed to the radon line (not shown in the diagram), pure radon frozen in the side-arm (a) immersed in liquid air, and stopcock s_1 closed. Then the vessel was transferred to the supply line and filled with acetylene through s_1, after which (with s_1 closed) it was sealed to the light absorption system shown in figure 1. The volume of container A is 4.6 times as great as the volume of the trap system plus the absorption system. High vacuum was obtained by means of mercury vapor pumps.

First the presence of benzene in the polymerizing acetylene was demonstrated. A mixture of 62 cm. of acetylene and 40 millicuries of radon was kept in A for seven days, after which time the gas was allowed to expand into the absorption system. During this interval considerable cuprene had been formed. The total pressure (in the volume including container A, the series of traps between stopcocks s_1 and s_2, the absorption tube and intervening tubing up to s_3) was 41 cm. as read on the mercury manometer M adjusted to a fixed point by leveling reservoir L. This is equivalent to a pressure of 50 to 51 cm. in A alone. Photograph No. 1 on the accompanying plate, the absorption spectrum of the expanded gas, is indisputably the spectrum of benzene vapor. Comparison with photographs 2, 3, and 4, which show the absorption spectra of benzene vapor[3] (supplied by liquid benzene in B) at pressures of 1.3 mm., 4.5 mm., and 2.5 cm. respectively, indicated the presence of more than 4.5 mm. of benzene in the reaction mixture. After the exposure, the gas was transferred to A by freezing in side-arm a and closing s_1.

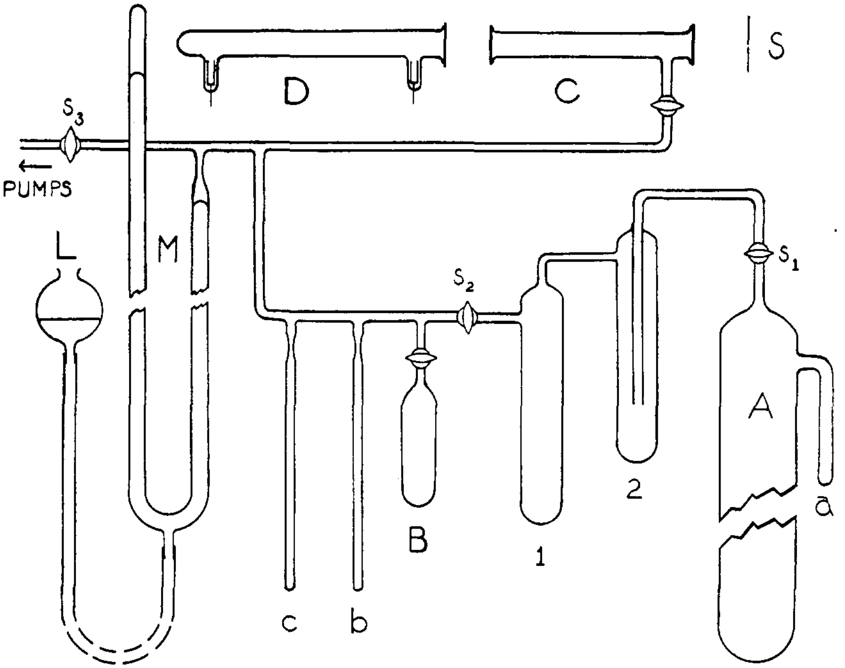

FIG. 1. The apparatus

To see whether appreciable quantities of other substances, which do not absorb in the region examined, are produced, the reaction mixture was passed twice through a carbon dioxide–acetone freezing mixture. Trap 1 was immersed in liquid air and trap 2 in the carbon dioxide plus acetone,

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[3] Spectra 2, 3, and 4 are but three of many such photographs taken at various pressures of benzene vapor.

after which stopcock s_1 was opened. When all the acetylene plus radon had condensed in 1 as indicated by M, the liquid air was transferred from trap 1 to side-arm a, and these gases collected in A. Presumably all substances which melt above about −70°C. were retained in trap 2. With s_1 and s_2 closed, the carbon dioxide–acetone recipient was removed, to reveal a thin deposit of a white crystalline solid which melted only after ten to fifteen minutes but which appeared to melt rather sharply. Droplets of liquid were observable on melting, although the liquid then vaporized, pointing to a rather high degree of volatility. By this procedure, the sensitivity of the examination is increased almost sixfold, since the container A is no longer a part of the space into which the vapor expands.

Connection was made with the absorption tube through s_2, and spectra 5, 6, and 7 photographed at pressures of 2.6 mm., 1.15 cm., and 2.7 cm., respectively, of vaporized liquid. Qualitative visual comparison with the benzene spectra (2, 3, and 4) pointed to partial pressures of benzene equal respectively to < 4.5 mm., < 2.5 cm., and 2.5 to 3.0 cm. In the absence of photometric observations, we are forced to conclude that the principal compound present in this liquid is benzene. The product was frozen in tube b, sealed by fusing the glass at the constriction, and preserved as a liquid (0.2 cc.) for future examination. The liquid was frozen by immersing the tube in a bath at −15°C., and then allowed to warm up slowly. The solid form melted between 6° and 7.5°C. This admittedly approximate measurement again points to the presence of benzene.

The demonstration was repeated with an initial acetylene pressure (in container A) of 85 cm. and 100 millicuries of radon. Five days after the mixture was introduced into A, the higher melting product was separated by freezing in the carbon dioxide–acetone paste as described above, and the absorption spectrum photographed (No. 8) at a pressure of 4.7 cm. Visual comparison with the spectra of pure benzene indicated the presence of more than 3 cm. Again we are led to believe that the product is chiefly benzene. This liquid was preserved by sealing in tube c.

An attempt was made to ascertain whether the benzene was produced by a reaction secondary to cuprene formation or whether it is an intermediate compound necessary to the production of cuprene. With this end in view the acetylene plus radon, freed from "benzene" and collected in container A after the first experiment, was permitted to stand for more than a month, after which time the decay of radon is practically complete and further polymerization has ceased. The initial pressure was thus about 48 cm. and the initial radon 11 millicuries. Stopcocks s_1 and s_2 were opened, thereby permitting the residual gas to expand into the evacuated absorption tube, and the spectrum photographed at a total gas pressure of 37 cm. (equivalent to 45 cm. in A). Again the absorption spectrum was that of benzene.

To make the test more sensitive, condensible products were frozen in trap 2 immersed in carbon dioxide–acetone, and the remaining gases collected in container A. A small pressure of 0.3 mm., presumably due to hydrogen (8), was observable even with side-arm a immersed in liquid air. After pumping off this permanent gas, the liquid air was transferred to trap 1, and the gas mixture again distilled through the carbon dioxide-acetone mixture. The acetylene was collected elsewhere and the carbon dioxide freezing bath removed. A thin film of solid was again in evidence. After melting and evaporation, connection was made with the absorption tube, and the spectrum photographed at a total pressure of 1.06 cm. of volatilized liquid. This spectrum (No. 9) corresponds to 0.6 to 0.7 cm. of benzene.

If we compare the yields of "benzene" for the two successive steps of the reaction, we find that the "benzene" production measured manometrically is proportional to the amount of radon decaying. Hence we must conclude that the reaction proceeds simultaneously with cuprene formation rather than being a step in the latter process. Table 1 shows the data pertaining to this calculation.

TABLE 1

Formation of "benzene"

Δt	RADON IN MILLICURIES	TOTAL PRESSURE OF "BENZENE"	$\frac{\text{"BENZENE" PRODUCED}}{\text{RADON DECAYED}}$
0	40	0	
7 days	11	2.7	0.093
> 1 month	0	1.06	0.096

Of course the acetylene used in these experiments was tested spectroscopically in the absence of radon. Spectrum 10 shows that no benzene vapor is present initially. In fact it is indistinguishable from the continuum (15 min. exposure) of the hydrogen lamp (No. 11). The iron arc is not shown.

It was found furthermore that benzene formation occurred under the influence of β-γ radiation as well. A cylindrical vessel similar to A, filled with stock acetylene but containing no radon, was placed 5 cm. from A. It is known (13) that β-radiation will cause acetylene to polymerize to cuprene. Actually the latter was observed in our vessel. In addition benzene was found to be present. Twelve days after placing the vessel near container A (with 100 millicuries of radon), the contents were permitted to expand into the absorption tube, and photograph 12 obtained at a pressure of 53 cm. in the entire system (container, traps, and absorption tube). This spectrum corresponds to about 1 mm. of benzene. The

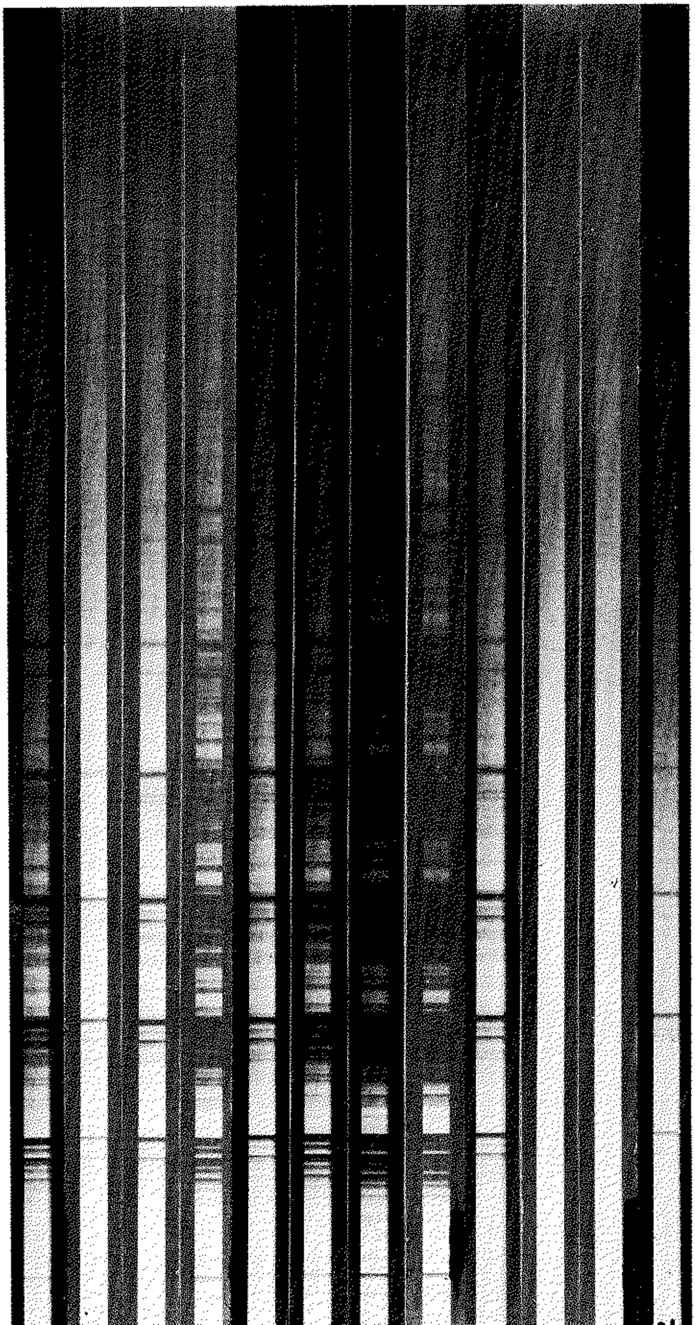

FIG. 2. Absorption spectra

mechanism of the β-γ ray reaction thus appears to be the same as that of alpha-ray reactions.

Further experiments now in progress are designed to determine the relative velocities of benzene and cuprene formation, as well as the composition of the liquid product. Consequently a detailed discussion will be postponed until this project is terminated.

SUMMARY

Absorption spectra of acetylene polymerizing under the influence of radon were photographed. By this means the formation of benzene was demonstrated for both the alpha-ray and the beta-gamma ray reactions. That cuprene is not the only polymer produced in appreciable quantities was shown by freezing out in a carbon dioxide–acetone mixture a solid which proved to be a volatile liquid at room temperature. This liquid was chiefly benzene. It appears as a result of a reaction proceeding simultaneously with cuprene formation.

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