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The Radiation Chemistry of Acetylene

I. Rare Gas Sensitization. II. Wall Effect in Benzene Formation[1,2]

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INTRODUCTION

In the radiolysis of acetylene, polymerization to form cuprene (*1*) and cyclization to form benzene (*2*, *3*) account for virtually all the reacted acetylene. At low conversion, 21 % of the acetylene forms benzene, and it has been shown (*3*) that the ratio of cyclization to polymerization is independent of pressure over a substantial range above 100 mm, and of absorbed radiation intensity. The indication from this kinetic study was that the reaction involves a complete duality of primary process in which the transient precursors of the benzene and the polymer are distinct and do not interact with each other in any way. This is in contrast with an earlier suggestion (*2*) that the polymer and the benzene originate from a common trimer intermediate.

The proposal was made that the separate primary processes might involve ionization on the one hand and electronic excitation by electron impact on the other, the primary precursor of benzene being an excited acetylene molecule, possibly in a triplet state. This speculation seemed the more inviting on the basis of published (*4*) data on the excited states of acetylene, the lowest of which was found to have molecular constants almost identical with those of benzene.

To obtain evidence bearing on the possible role of electronic excitation in the cyclization, an investigation of the rare gas-sensitized radiolysis of acetylene, with a special emphasis on benzene formation in the helium-sensitized reaction, has been carried out. The radiation sensitization of the acetylene polymerization by rare gases in mixtures with acetylene has long been known from the classic studies

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[1] Based on a paper presented before the annual meeting of the Radiation Research Society, Pittsburgh, May 18–20, 1959, as part of the Symposium on Radiation Chemistry of Gases in honor of Dr. S. C. Lind on the occasion of his eightieth birthday. The Symposium was organized by Dr. Leon M. Dorfman, and he and Dr. A. O. Allen served as chairmen of the sessions.

[2] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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of Lind and his collaborators (*5*). The present study was undertaken on the basis of the following consideration. In the helium-sensitized radiolysis there is an important difference in the primary process as compared with the direct radiolysis in which both ionization and excitation can, of course, take place. Since the sensitization involves energy transfer to acetylene from either a helium ion or an excited helium atom, it can be readily seen that the result in either case will be ionization of the acetylene. If the collisional transfer is from a helium atom in the 2^1P or 2^3P state, or the metastable 2^1S or 2^3S state, and the helium returns to the ground 1^1S state, then ionization of the acetylene will occur, since all excited states have energies in excess of 19.7 ev (*6*), and the ionization potential of acetylene is 11.4 volts (*7*). There is, in fact, direct experimental evidence (*8*) of the ionization of acetylene by excited helium atoms. Collision with ^1P or ^3P atoms with transitions to the lower-lying S states cannot produce electronic excitation of the acetylene, since transitions from the higher S and P terms to the $2S$ and $2P$ states all involve less than 4.7 ev, which is probably insufficient to raise the acetylene molecule to its lowest excited state. Therefore only ionized states of acetylene will be formed in the sensitization by excited helium atoms. If collision with helium ions occurs, then charge transfer will ionize the acetylene, the ionization potential of helium being 24.6 volts (*9*).

Thus, in the helium-sensitized radiolysis of acetylene, electronically excited neutral acetylene is eliminated as a primary transient, an ionized state of acetylene always resulting from the collisional transfer. If an excited neutral acetylene molecule is indeed the primary precursor of benzene, then the cyclization reaction should be eliminated in the helium-sensitized radiolysis.

In addition to the helium-sensitized radiolysis, sensitization by argon, krypton, and xenon has also been examined. The work with helium led, of necessity, to an investigation of the direct radiolysis in the low-pressure region for the following reason. To preserve the condition helium $\gg$ acetylene in order that the electron fraction of helium should be very much greater than that of acetylene in the sensitized runs, it was necessary to use low pressures (ca. 7 mm) of acetylene, and for comparison purposes the formation of benzene in the direct radiolysis in this pressure region had also to be determined.

EXPERIMENTAL PROCEDURE

The preparation and purity of the gases used was as follows. Matheson Co. acetylene was degassed at −150°C and then subjected to distillation three times at −125°C. Mass spectrometric analysis disclosed no impurities, which therefore amounted to certainly less than 0.1 %. Helium from three separate sources was used. In some runs, ordinary tank helium was used without further purification. In two runs, research-grade helium, obtained from Air Reduction Co., was used. Analysis of this helium showed the following: nitrogen 0.05 %, oxygen 0.01 %. In six other runs, tank helium was purified by bubbling it through a column of sodium-potassium alloy specifically to remove oxygen which might conceivably have an inhibitory effect. Analysis of this purified helium showed: oxygen <0.004%; nitrogen <0.017%. The argon, krypton, and xenon were all research-grade gases, obtained from Air Reduction Co., and were used without further purification. Analysis of these gases showed the following impurity content: the argon contained 0.06% nitrogen, 0.01% oxygen; the krypton contained <0.15% nitrogen, <0.01% oxygen; the xenon contained 0.13% nitrogen, <0.01% oxygen.

The source of radiation was a Van de Graaff accelerator delivering a 1-Mev electron beam. The electron beam entered the reaction cell through a 2-mil-thick stainless steel window so that the peak energy of the electrons incident on the gas was approximately 0.8 Mev. Beam currents of 30 to 60 μa were used, the majority of runs being carried out at about 55 μa. At these currents, with the cell window 1½ inches below the accelerator window, the required irradiation times ranged from ½ minute in some of the sensitized runs to 45 minutes in the low-pressure direct radiolysis.

Glass reaction cells of two different sizes were used. Two cylindrical cells with a window at one end, with inside diameter 35 mm, over-all length approximately 18 cm, and total volume 165 cc, were used in most of the runs. A large spherical cell, total volume 1031 cc, consisting of a 1-liter bulb connected to a 30-mm fernico seal to which the stainless steel window was fastened, was used in a series of runs. The precise volume ratio of these cells was 6.25. The condition of the reaction cell wall was not identical in all the runs. The change in surface condition resulted from the deposition, during each run, of a very thin layer of cuprene polymer, for which there is no known solvent. For six runs (the initial pair and two subsequent sets before which the cell was opened) the surface was completely clean at the start of the irradiation. For another six runs the polymer layer was rather incompletely removed by the mechanical action of water, and the cell was subsequently degassed. In the remainder the surface had accumulated a polymer layer of varying thickness. The reproducibility of the results regardless of the previous history of the surface indicated quite clearly that the reaction rates were unaffected by the condition of the surface.

The benzene analysis was performed spectrophotometrically with a Cary recording spectrophotometer, Model 14R, by measuring the 2530-A benzene absorption in the gas after each run. The absorption spectrum from 2300 to 2700 A was recorded after each run with a 10-cm absorption cell, and in addition the 2530-A peak was separately recorded by using the slowest scan rate and highest sensitivity of the instrument. The limit of sensitivity of the analysis was somewhat better than 0.1 μM of benzene. The amount of benzene formed in the direct radiolysis in the small cells usually exceeded 0.8 μM, and in the spherical cell it was usually greater than 4 μM. Although it was necessary to establish only the linearity with pressure of the benzene absorption curve, and thus to determine the relative amounts of benzene for purposes of this investigation, an absolute calibration was nevertheless carried out in the following way. At the high end of the pressure range a known pressure of benzene was introduced directly into the absorption cell, and the 2530-A peak measured. In the lower range where this method was not feasible, known quantities of benzene were formed in direct radiolysis runs at higher acetylene pressure, where the fraction of acetylene going to benzene is known (*3*) with moderately good accuracy, and introduced into the absorption cell. From these measurements, calibration points on the same absorption curve were obtained.

The amount of acetylene reacting was determined simply by measuring the initial and final pressures on a manometer which was read with a cathetometer. The minute amounts of hydrogen formed were, of course, removed before the final pressure reading was taken. In runs at the lower acetylene pressures these readings were taken in a small analytical volume (ca. 9 cc) into which the acetylene had been condensed. In order to minimize any possible loss of benzene, the stopcocks in this part of the vacuum system were lubricated with silicone grease. In the sensitized runs the rare gas was very slowly pumped off after the run through two traps, at −195°C, in which the condensables, acetylene and benzene, were trapped. After reading the final pressure the entire condensable fraction was condensed into the ultraviolet absorption cell for measurement. In the xenon-sensitized runs the rare gas was not pumped off before reading, but the final and initial pressures were measured for the total of xenon and acetylene.

RESULTS AND DISCUSSION

Benzene Calibration

The calibration curve for benzene analysis by measurement of the ultraviolet absorption at 2530 A, over the range 1 to 12 μM of benzene, is shown in Fig. 1. The ordinate represents the optical density, and the abscissa the amount of benzene present in the ultraviolet absorption cell, which has a volume of 30.0 cc. The solid circles represent points obtained by introducing a known pressure of benzene directly into the ultraviolet absorption cell. The remainder of the points were obtained from runs at moderately high pressure, for which the amount of benzene was calculated on the basis of the previously determined (*2*, *3*) 21% conversion of acetylene to benzene.

The optical density is linear, or at least very nearly so, in the benzene pressure so that the 2530-A peak height is an adequate representation, for the purpose of the present investigation, of the amount of benzene formed. It should be understood that the interpretation of the results of this investigation is not dependent on the absolute calibration for benzene, a relative determination of benzene forma-

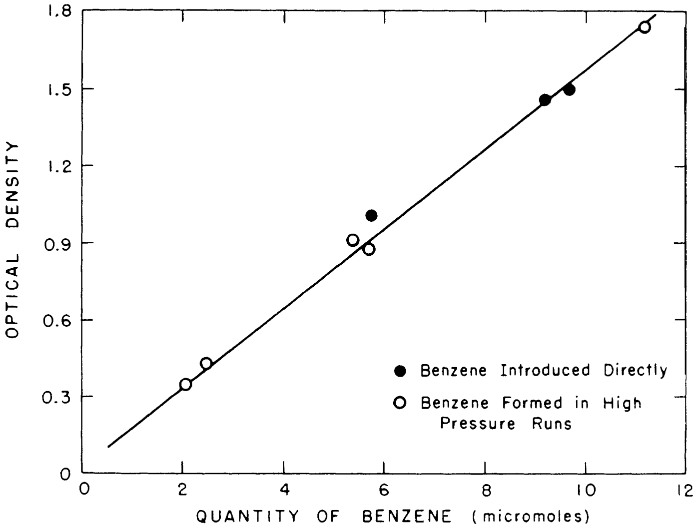

FIG. 1. Calibration for benzene analysis by ultraviolet absorption at 2530 A.

tion being sufficient. Nevertheless the absolute calibration is useful for purposes of reference. The calibration constant, obtained from Fig. 1, for the optical density per micromole of benzene is 0.165 ± 0.011. That is, a peak height of 16.5 chart divisions is obtained for 1 μM of benzene, and the sensitivity of the measurement is approximately 0.07 μM.

Rare Gas Sensitization

The details of ten runs on the helium-sensitized radiolysis using the cylindrical cells are shown in Table I. The data in the table show the initial pressure of acetylene and the pressure of helium, the electron fraction of helium, the diminution in acetylene pressure, and the number of moles of acetylene reacting. In analyzing for benzene several runs were combined in the ultraviolet absorption cell to increase the quantity of benzene, if any were formed. These combined runs are indicated in the table by brackets and consisted of runs 8 and 9, 19 and 21, and 26 through 29. The results of the benzene analysis may be summarized by stating that no benzene was detected in any of these runs, with the possible exception of the combination of the last four, in which a total of 71 μM of acetylene reacted, and for which an absorption was barely discernible. It is clear, therefore, that in the helium-sensitized radiolysis of acetylene, in contrast with the direct radiolysis, cyclization to benzene is essentially eliminated, as anticipated on the basis of the reasoning set forth in the Introduction.

In addition to the helium-sensitized radiolysis, sensitization by argon, krypton,

TABLE I

HELIUM-SENSITIZED RADIOLYSIS OF ACETYLENE

Run No.	*Pressure (mm)*		*Electron fraction of helium*	$-\Delta P_{C_2H_2}$ *(mm)*	C_2H_2 *reacting (moles* × 10^6*)*
	Acetylene	*Helium*			
8	7.20	675	0.93	1.93	17.2
9	7.20	675	0.93	1.84	16.4
11[a]	6.83	590.3	0.93	2.28	20.4
12[a]	6.83	590.3	0.93	2.07	18.5
19[a, b]	7.99	661.9	0.92	2.12	15.5
21[a]	5.87	523.2	0.93	1.65	14.7
26[a, b]	7.54	603	0.92	2.29	16.7
27[a, b]	7.54	603	0.92	2.66	19.4
28	7.43	534	0.91	2.01	17.9
29	7.43	492	0.90	1.94	17.3

[a] Helium purified through NaK column.

[b] Cylindrical cell of slightly smaller volume, 135 cc, used in these runs.

TABLE II

RARE GAS-SENSITIZED RADIOLYSIS OF ACETYLENE

Run No.	*Pressure (mm)*		*Electron fraction of rare gas*	$-\Delta P_{C_2H_2}$ *(mm)*	C_2H_2 *reacting (moles* × 10^6*)*	*Benzene formed (moles* × 10^6*)*
	Acetylene	*Rare gas*				
36[a]	34.24	170 A	0.86	5.88	42.9	0.1
37[a]	34.24	170 A	0.86	5.83	42.6	0.1
54	23.21	127.9 A	0.88	7.81	69.6	0.1
15	23.10	245.8 Kr	0.96	2.8	25	0.1
13	29.48	117.7 Xe	0.94	2.2	20	0.1
53	22.13	108.2 Xe	0.95	4.53	40.4	0.2

[a] Cylindrical cell of slightly smaller volume, 135 cc, used in these runs.

and xenon has also been examined for benzene formation. The results of six runs with these rare gases are shown in Table II. The figures in the last column show that barely measurable quantities of benzene were formed, rather than amounts of the order of 1 to 3 μM which would be formed in the direct radiolysis for the quantities of acetylene reacting in these particular runs. The very small amount of benzene which was formed is to be attributed to that small fraction of the incident energy which is absorbed directly by the acetylene and results in cyclization as well as polymerization. Otherwise it is clear that in the radiolysis sensitized by argon, krypton, and xenon, as well as by helium, the cyclization reaction is eliminated.

Pressure Dependence and Wall Effect in the Direct Radiolysis

It seemed advisable, for comparison purposes, to have data on benzene formation in the direct radiolysis at the low acetylene pressures used in the helium-sensitized radiolysis. This was particularly so in view of the fact that no benzene at all was detected in most of the helium-sensitized runs, whereas on the basis of a 21 % conversion to benzene for that fraction of the acetylene which reacts as a result of direct absorption of energy, rather than by sensitization, a detectable quantity would have been expected.

The results of a series of twenty-five runs demonstrate that the rate of benzene formation in the direct radiolysis does indeed decrease with decreasing pressure in the low-pressure region. There is no need to tabulate the details of all these runs, since the over-all result is quite adequately represented in Fig. 2. Nevertheless the details of a few of these runs are shown in Table III. The amount of acetylene reacted was such that the quantity of benzene formed in these runs ranged from 0.6 to 5.5 μM with the cylindrical cells, and was as high as 10 μM with the large spherical cell. At the lowest pressure used with the cylindrical cells, the products of four separate identical runs were combined for ultraviolet analysis to bring the amount of benzene formed to 1.2 μM.

The data are shown in Fig. 2, in which the fraction of the reacted acetylene which forms benzene is plotted as a function of the initial acetylene pressure. The open circles are for runs in the cylindrical cells. The fraction of acetylene forming benzene,

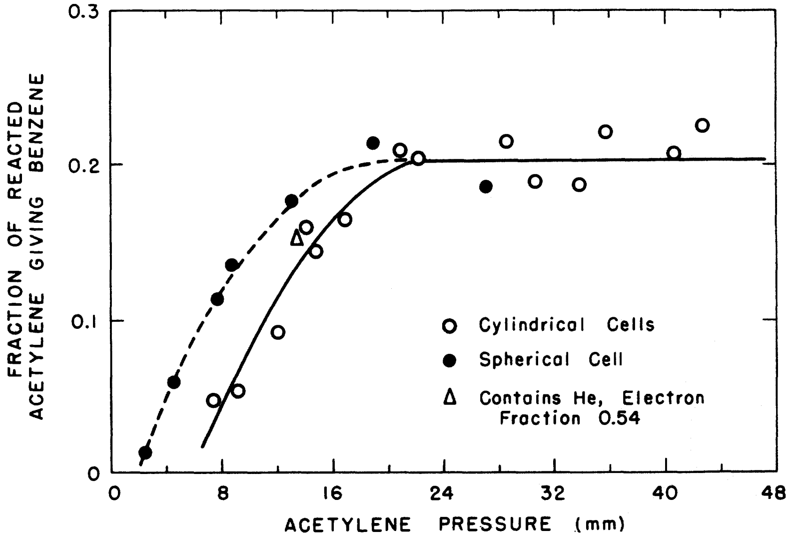

FIG. 2. Pressure dependence and wall effect in benzene formation in the direct radiolysis of acetylene.

TABLE III

BENZENE FORMATION IN THE DIRECT RADIOLYSIS—TYPICAL RESULTS

Run No.	*Acetylene pressure (mm)*	*Pressure decrease (mm)*	*Acetylene reacting (moles* $\times$ *10⁶)*	*Benzene formed (moles* $\times$ *10⁶)*	*Fraction of reacted acetylene forming benzene*
14	40.72	7.99	76.9	5.5	0.21
66	12.06	1.91	17.8	0.58	0.098
60[a]	4.59	0.83	47.3	1.02	0.065
74[a]	13.06	1.86	110.5	6.7	0.18

[a] Large spherical cell used in these runs.

which has been shown (*3*) to be invariant with pressure at higher pressures, maintains its value of 0.2 down to the region around 20 mm. With further decrease in pressure it is clear that the fraction forming benzene begins to fall off quite sharply, reaching a value of approximately 0.04 at a pressure of 8 mm. There is one point on this curve (indicated by a triangle) which represents a run containing a small amount of helium, the electron fraction of helium being only 0.54 for this run. The fraction of reacted acetylene going to benzene has been calculated for only that part of the energy which has been directly absorbed by the acetylene. As may be seen, the point lies very close to the curve. The estimate of directly absorbed energy based on electron fraction would, if anything, be slightly low, so that the point would lie even closer to the curve than is indicated.

The decrease in benzene formation at the lower pressures (in contrast with its invariance over an extensive range of increasing pressure) can be logically attributed to a wall effect. If one of the transient precursors of the benzene, either monomer or dimer, has a sufficiently long lifetime, it will diffuse to the wall where it may be deactivated before the trimer can be formed. It seems unlikely that the trimer transient would have a sufficiently long lifetime to diffuse to the wall, since only a molecular rearrangement would be required to form benzene. This diffusion-dependent deactivation will then compete with benzene formation at low pressures as determined by the transient lifetime and the mean path length to the walls. The evidence which establishes that such an explanation is substantially correct was obtained from the runs with the spherical cell for which the mean path length to the walls is considerably greater than for the cylindrical cells. The average distance to the walls for this cell—0.75 times the radius (*10*)—is approximately 4.5 cm, whereas for the small cylindrical cells it is considerably less, probably between 2 and 3 cm. The solid circles in Fig. 2 represent runs with the spherical cell. The decrease in benzene formation is again observed, but the curve is now significantly shifted to lower pressures as expected, because of the longer time of diffusion to the walls.

From these observations it is possible to draw some interesting and important conclusions about the characteristics of the benzene precursors. The root-mean-square molecular velocity at 25°C is approximately 5×10^4 cm sec^{-1} for a molecule having the mass of the monomer, and 3.3×10^4 cm sec^{-1} for the dimer mass. Since the average distance to the wall is 4.5 cm, we can conclude that the lifetime of one or both of these transients is at least 10^{-4} sec and may be considerably greater, since the mean path length to the walls is certainly greater than the average distance. If these transients are electronically excited states of acetylene or of the dimer, this would rule out the singlet state as a possibility, since the radiative lifetime for the singlet is more than three orders of magnitude too short. The following is also noteworthy. At a pressure of 10 mm the collison frequency at 25°C would be approximately 8×10^7 sec^{-1}. Thus, on the average, the transients must survive at least 8000 collisions with acetylene molecules in the ground state in order to reach the walls. This means that the elementary reactions involved in the cyclization do not have the characteristics normally attributed to ion-molecule reactions which apparently occur with high cross section and unity collision efficiency. The reasonable possibilities are an excited molecule in a triplet state or perhaps a free radical.

It is of interest to compare this pressure effect on benzene formation in the radiolysis of acetylene with the analogous data from the photochemical reaction. The photochemical studies show that in both the photolysis (*11*) at 1849 A and the mercury—photosensitized reaction (*12*) the quantum yield for benzene formation does indeed fall off at low pressures. In the photolysis it begins to decrease at 25 to 30 mm, and it has decreased more than tenfold at 2 mm; in the photosensitized reaction it declines sharply below 20 mm. There is, however, a striking difference in these photochemical studies as contrasted with the radiolysis, in that the quantum yield for polymerization shows an identical decline at low pressures, the fraction of acetylene going to benzene remaining constant down to a few millimeters, the lowest pressures investigated. From the present investigation it is clear that in the radiolysis the polymerization yield does not show a decrease corresponding to that of the cyclization at low pressures. It may be that the polymerization yield does not decrease at all at lower pressures, but this cannot be shown definitively from the present investigation because of an uncertainty, owing to the contribution of the slow electron component of the scattered secondaries, in calculating the relative absorbed intensity at lower pressures.

From these new observations (1) that benzene formation is eliminated in the rare gas-sensitized radiolysis of acetylene, whereas the polymerization yield is apparently unchanged (*5*), and (2) that the benzene yield is sharply reduced at lower pressures owing to a wall effect, taken together with the earlier kinetic studies (*3*), it seems a reliable conclusion that the acetylene radiolysis involves at least a duality of primary process. A consideration of the conditions under which the wall effect is manifested indicates the likelihood that the transient precursors of the benzene are excited molecules in a triplet state. On the basis of these observations and the foregoing discussion, the suggested mechanism for the direct radiolysis involves ionization:

$$C_2H_2 + e = C_2H_2^+ + 2e \tag{1}$$

which may result in polymerization through a series of ion-molecule reactions:

$$C_2H_2^+ + C_2H_2 = C_4H_3^+ + H \tag{2}$$

which have been observed (*13*,*14*) in the mass spectrometer; or, as well, by means of a free radical chain which may be initiated by either ionization or excitation:

$$H + C_2H_2 = C_2H_3 \xrightarrow{C_2H_2} \text{Polymer} \tag{3}$$

Cyclization occurs quite independently as a result of electronic excitation by electron impact:

$$C_2H_2 + e = C_2H_2^* + e \tag{4}$$

$$C_2H_2^* + C_2H_2 = (C_2H_2)_2^* \xrightarrow{C_2H_2} C_6H_6 \tag{5}$$

In the sensitized radiolysis ionization by charge transfer occurs, leading to polymerization. Dissociative ionization apparently occurs to only a small extent in both the direct ionization (*15*) and the charge transfer ionization (*14*).

SUMMARY

In the rare gas-sensitized radiolysis of acetylene, with helium, argon, krypton, and xenon, cyclization to benzene, an important process in the direct radiolysis, is completely eliminated. In the direct radiolysis the fraction of reacted acetylene going to benzene, which is constant at 0.2 at high pressures, is found to decrease sharply at very low pressures. This is shown to be due to a wall effect. From a consideration of the experimental conditions it is shown that benzene precursors reaching the wall have a lifetime of at least 10^{-4} sec.

These new observations, together with the earlier kinetic studies, are consistent with a mechanism involving a complete duality of primary process in which the precursors of the polymer and of benzene are distinct. It is suggested that ionization of the acetylene leads to polymerization, whereas cyclization requires electronic excitation of the acetylene, probably to a triplet state.

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