# **RADIATION CHEMISTRY OF PURE ORGANIC** COMPOUNDS: BENZENE AND BENZENE-d<sub>6</sub>\*

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In this paper we attempt the use of mass spectrometric and radiation chemical data on the same compounds for interpretation of mechanism of their decomposition. Mass spectrometric data on organic compounds reveal a large number of ions, including many formed by rearrangement from highly excited ions. Products formed by radicals complementary to the ions have been found in radiation chemistry. Some effects of impingent particle velocity interpretable in terms of energy transmitted to the individual molecule have also been reported. Energy may be transferred to surrounding molecules or within a molecule so as to favour one type of decomposition and prevent another. In such energy transfer process mechanisms, the same entity may act as both donor and recipient. When ionization and excitation potentials are greatly different the component of a mixture of lower ionization or excitation potential can be a protective agent. In radiolysis of pure liquid C<sub>6</sub>H<sub>6</sub> and of pure liquid C<sub>6</sub>D<sub>6</sub>, by 1.5 MV electrons, yields of gaseous products are  $G(H_2) = 0.036$ ,  $G(C_2H_2) = 0.020$  and  $G(D)_2 = 0.0117$ ,  $G(C_2D_2) = 0.0133$ . Results of radiation chemistry as well as of mass spectrometric measurements indicate two mechanisms of decomposition, by bond rupture and by rearrangement. In a mixture the  $C_6H_6$  and  $C_6D_6$  protect each other against radiation. The general concept of protection is discussed in the light of these results.

1. FUNDAMENTALS OF THE RADIATION CHEMISTRY OF PURE ORGANIC COMPOUNDS

The phenomena of the radiation-chemical effects of a single high-energy photon or particle include primary and secondary ionization and excitation, charge and excitation transfer, and charge neutralization as well as internal conversion, decomposition processes and free-radical reactions are familiar to the photochemist. The unravelment of some of these phenomena is expedited by studies of organic systems because of the essential simplicity of properly selected organic compounds and because we may, if we wish, select compounds whose molecules (unlike those of water) are not chemically combined with each other. Furthermore, radiation chemists have varied molecular size and structure in a regular way and have thus obtained rather revelatory information about phenomena of great interest.

The primary processes of radiation chemistry are ionization and excitation. Ensuant thereon there may be negative-ion formation and there is always neutralization. The mass spectrometer used simultaneously as source of energy and analytical instrument has proven a very useful tool for elucidation of some of these processes, particularly such as occur in highly attenuated gases.<sup>1</sup>

VARIETY OF PRIMARY PROCESSES .--- The mass spectrometer indicates that a large number of ions and radical and molecule fragments may be formed in a primary step but with different appearance potentials. However, it must be emphasized that these observations are made on very attenuated gas. Detailed calculations on the basis of the Bethe equation <sup>2</sup> by Hentz <sup>3</sup> show that in an assumed

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condensed system of hydrogen atoms the energy goes with very high probability to yield the lowest excited and ionized states in ratio dependent on the energy of the incident particle involved. While such a calculation is by no means the last word on such a matter, it does indicate that in a liquid organic system the number of primary products may be considerably more limited than indicated by the mass spectrometer.

The mass spectrometer does, however, make certain facts clear. The parent ion is not necessarily the most abundant. This statement has been shown to be particularly true for fluorinated hydrocarbons, in which case Mohler *et al.*<sup>4</sup> have suggested the primary removal of an  $F^-$  ion. Mariner and Bleakney <sup>5</sup> have made similar electron impact studies on formic acid and have also suggested formation of a negative ion as one of the fragments.

Mass spectra frequently contain peaks corresponding to ion groupings not present in the parent molecule.<sup>6</sup> Such a result means only that in the time before the ion enters the accelerating field,  $10^{-7}$  sec, it may rearrange and dissociate into other ions. By a careful study of non-integral peaks many metastable ions with half-life of the order of  $10^{-6}$  sec have been revealed.<sup>7</sup> Such ions may decompose by rupture to yield other ions and radical fragments or may rearrange to give ions and stable molecules. The ions in the latter case need not be present as groupings in the parent ions. By use of a radiotracer technique, Williams and Gevantman <sup>8</sup> showed that some of the rearrangement fragments found in mass spectroscopy of aliphatic hydrocarbons are indeed produced as free radicals in an early stage of radiolysis of some of these compounds. The diversity of primary products was certainly greater than might be concluded from a necessarily simplified calculation from the Bethe equation.

Thus, in a rather fundamental way, it has already been shown in radiation chemistry that, in spite of the enormous energies available for excitation and ionization processes, the excited entities have a comparatively long life and may rearrange before decomposition.

FACTORS WHICH AFFECT RELATIVE FREQUENCY OF PRIMARY PROCESSES.—The mass spectrometer is not a good tool to reveal, for example, the effect of temperature on the relative frequency of occurrence of the various primary processes.<sup>9</sup> The relative peak heights are changed but such changes are caused by many factors not at all connected with an effect on relative probability of formation of ions. Such information can be obtained only by direct study of the radiation chemistry of compounds involved. Interpretation of the results in such case would be confused by the effect of temperature on possible subsequent free radical reactions.

Some effort has been made to find an effect of impingent particle velocity on the relative frequency of the primary processes. Such an effect is indeed existent in mass spectrometry, where the relative ion abundances are very sensitive to the voltage of the impingent electrons. However, the velocities and velocity differences are small and, indeed, trivial in comparison with the velocities of interest in radiation chemistry, namely the velocity of an alpha particle and the approximately 86 times greater velocity of a beta particle of the same energy. The only work reported on this point is indirect and is on liquid systems. Sworski and Burton <sup>10</sup> compared the effects of 1.5 MeV electrons from a Van de Graaff generator and mixed radiation from the Oak Ridge graphite nuclear reactor on a variety of aromatic compounds and obtained the results summarized in table 1.

TABLE 1.—Comparison of ratios of yields,  $H_2/CH_4$ , in radiolysis of some liquid hydrocarbons

compound	pile irradiation,	electron irradiation, e	p/e
toluene	25.9	16.4	1.58
ethylbenzene	9.7	5.9	1.64
iso-propylbenzene	4.2	2.3	1.83
tertbutylbenzene	3.5	1.6	2.09

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The effect of the slow-particle (neutron) bombardment in the reactor was attenuated by gamma radiation and the interpretation of effects was weakened by the choice of liquid compounds for this study. In the liquid state the possibility exists that cage effects will have special influence in slow-particle bombardment, where primary products are formed relatively close together. In some current studies by Dr. S. Schrage a clearer distinction will be sought by studies on methane gas containing radioiodine. In these experiments the relative gamma input in the reactor is markedly decreased by the use of suitable shielding.

CHARACTERISTIC CHEMICAL EFFECTS.—One of the most interesting aspects of radiation chemistry is the relative lack of reactivity of aromatic compounds compared to aliphatic.<sup>11</sup> In photochemistry, such a phenomenon is largely unrevealed, primarily because of high excitation potential of aliphatic compounds. However, high-energy radiation is absorbed equally well by both and gives a G value (i.e. yield of molecules per 100 eV input) of about 6 for the decomposition of aliphatic compounds and of about one-hundredth that figure for benzene. In general, in normal aliphatic compounds, the relative quantity and nature of the products produced is determined by the abundance and nature of the parent groups in the original molecule.<sup>11, 12</sup>

In a series of studies on fatty acids and other compounds, it was shown by Breger, Sheppard, Burton, V. L., *et al.*<sup>13</sup> that for larger molecules departures might be noted from the simple rule just cited. For example, radiolysis of palmitic acid led, on this basis, to a disproportionately high yield of pentadecane and carbon dioxide. An explanation suggested for this effect is that in the liquid state deactivation characteristic of a cage effect frequently lowers the excitation energy to a level sufficient only for a decomposition by rearrangement,<sup>14</sup> e.g.

$$C_{15}H_{31}COOH \rightarrow C_{15}H_{32} + CO_2.$$

However, as has been pointed out,<sup>15</sup> such an explanation is inadequate to explain all the curious effects reported. Special structure of the molecules and the interrelation of the different groupings are also very much involved.

ENERGY TRANSFER WITHIN MOLECULES.—Comparative studies of the photochemistry and radiation chemistry of a group of alkyl-substituted benzenes (toluene, mesitylene, and ethyl, sec.-propyl, and tert.-butyl benzenes)<sup>16</sup> have shown that energy absorbed in the benzene ring is transmitted with low probability to the side groups, which decompose preferentially at a bond once removed from the ring, and that energy absorbed initially in the side groups may be transmitted into the ring. The energy held in, or transferred into, the ring is not very effective for decomposition. Studies of the radiation chemistry of pure liquid benzene indicate that the yields of hydrogen and acetylene do not exceed values corresponding to  $G(H_2) = 0.036$  and  $G(C_2H_2) = 0.022$ <sup>17</sup> and this non-reactivity appears to persist in the substituted compounds. The actual transfer of energy within a molecule, by a process of internal conversion, is well known from photochemistry. This particular series of studies showed not only that the recipient group could be thereby decomposed (a well-known phenomenon) but also that the recipient group might protect an essentially more reactive group from the effects of the energy it absorbed.

ENERGY TRANSFER BETWEEN MOLECULES.—In radiation chemistry energy transfer involves both excitation transfer (common in photosensitization processes of photochemistry) and ion transfer. Such transfer processes may be important in mixtures. Provided the states produced by the initial excitation are sufficiently persistent, ionization may be transferred from a molecule of higher ionization potential to one of lower <sup>18</sup> and the latter would thereafter act as if it had been the one initially ionized. The condition for excitation transfer is formally similar. The recipient molecule must have an energy state not too much different in content from that of the donor molecule.<sup>19</sup> After energy transfer, the recipient molecule may lose a portion of its energy in collisional processes and even transfer energy back to the donor molecule. Ultimately, if the recipient molecule has a sufficiently low excited state its properties and reactivity largely determine the observed chemical effect in the mixture—so far as it is caused by excitation.<sup>17</sup>

The total chemical effects in a mixture are the resultant of a number of effects including both excitation transfer and ionization transfer. It is possible, with the right relationship of energy levels, that the two effects might actually oppose each other but such opposition does not imply absence of mutual effect. Indeed, it is possible to have mutual protection of the constituents of a mixture, as in the liquid mixture of benzene and cyclohexene,<sup>11</sup> which have very nearly the same ionization potentials.<sup>20</sup> It has been shown by Manion and Burton <sup>17</sup> that, provided the  $G(H_2)$  values for the two separate components, A and B, of a mixture are sufficiently different, the combined  $G(H_2)$  value is given by a simple relation

$$G(H_2) = \frac{fN_A G(H_2, A)}{(1 + bN_B)(fN_A + N_B)} + \frac{N_B G(H_2, B)}{fN_A + N_B},$$
(1)

where  $G(H_2, A)$  and  $G(H_2, B)$  are the  $G(H_2)$  values for the pure separate components,  $N_A$  and  $N_B$  are the respective mole fractions, b is an experimental constant and f is the ratio of "electron numbers" of molecules A and B. Eqn. (1) has been shown to be consistent with the simple energy transfer mechanism but it cannot be said that the mechanism has been unequivocally established.

#### 2. Benzene and Benzene- $d_6$

One of the difficulties in the interpretation of radiation-chemical studies of benzene derivatives and benzene mixtures is the uncertainty regarding the mechanism of decomposition of benzene and particularly whether free radicals or ultimate molecules are formed in the primary act. There is some information based on bleaching of molybdenum trioxide by benzene gas exposed to light of  $\lambda < 2150$  Å that atomic hydrogen is produced by excitation processes.<sup>21</sup> The formation of one part of ethylene and two parts of acetylene in radiation-chemical decomposition of benzene vapour has been interpreted in favour of the free-radical mechanism in that case.<sup>17</sup> No other information bearing on detailed mechanism exists.

For elucidation of the mechanism of the photochemical and thermal decomposition of acetaldehyde, it has proved very useful to study a mixture of acetaldehyde and acetaldehyde- $d_4$ .<sup>22</sup> In this work, we have used a similar (but not so extensive) procedure in the study of benzene and benzene- $d_6$ . Furthermore, we have determined the mass-spectrometer pattern of benzene- $d_6$  and have compared it with that of ordinary benzene for elucidation of the mechanism of some of the early steps in the ionization portion of the decomposition.

### EXPERIMENTAL

MATERIALS AND HANDLING.—Benzene, Merck & Co. reagent grade, thiophene-free, was distilled through a 100-theoretical-plate column and the middle fraction boiling at  $80.0^{\circ}$  C was collected. On subsequent fractional crystallization, the crystals from the fourth freezing were retained;  $n_{b1}^{21} = 1.4999$ . Benzene- $d_6$  was synthesized by Dr. T. J. Sworski according to the method of Ingold,

Benzene- $d_6$  was synthesized by Dr. T. J. Sworski according to the method of Ingold, Raisin and Wilson <sup>23</sup> (i.e. by four successive equilibrations of benzene with 51 mole % D<sub>2</sub>SO<sub>4</sub> in heavy water <sup>24</sup>). The sample used had a deuterium content as determined by mass spectrometry of greater than 99 %, corresponding to 5.6 mole % C<sub>6</sub>D<sub>5</sub>H impurity. The benzene and benzene- $d_6$  were degassed, dried over sodium, and used to fill the

The benzene and benzene- $d_6$  were degassed, dried over sodium, and used to fill the irradiation cells according to the "vacuum-filled" technique described by Manion and Burton.<sup>17</sup> The reagents were never distilled through joints or stopcocks lubricated with vacuum grease. Break-offs and glass seals were employed for all gas transportation. The samples were never exposed to the atmosphere after the initial degassing and drying.

IRRADIATION CELLS.—Cells used in irradiation were similar to those described by Hentz and Burton  $^{16}$  except that the windows were ground glass of 5 mils thickness (contrasting with 0.014 to 0.018 in. previously used). The window diameter was 0.9 cm.

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IRRADIATION PROCEDURE.—Technique of irradiation was like that of the previous work of this kind <sup>17</sup> except that cells were cooled with an air stream rather than with dropping water. During runs the current was made constant at 1.5 MV and  $2.0 \pm 0.1 \mu$ A. For calculation of the amount of energy dissipated in the liquid contents of a cell a correction of 3 % was applied for energy absorbed in the cell window.<sup>16</sup>

PRODUCT DETERMINATION.—After irradiation, the cell was attached to a vacuum line for extraction and separation of the gaseous contents into two fractions: one noncondensible over liquid nitrogen ( $-196^{\circ}$  C) and the second non-condensible over ethyl bromide mush ( $-120^{\circ}$  C). Volumes of gas in these fractions were determined by the semi-micro method of Saunders and Taylor.<sup>25</sup> The two separated gas fractions were transferred to glass containers and analyzed on a mass spectrometer for chemical and isotopic composition. They were essentially pure hydrogen and acetylene respectively; no methane was present in the  $-120^{\circ}$  fractions.

Mass spectra of benzene and benzene- $d_6$  as well as of products of irradiation of pure benzene were run with a Consolidated 21-102 instrument under the supervision of Mr. Richard Wertzler in the Research Laboratories of the Sinclair Refining Co. at Harvey, Illinois. Product analysis of samples from benzene- $d_6$  and from the 0.50 electronfraction samples were run on a 21-103 instrument at Pasadena by Consolidated Engineering Corporation. Certain acetylene results were rejected by us because of evident contamination *en route*. One sample of product from benzene- $d_6$  and all other samples not specifically mentioned were analyzed on our own  $60^\circ$  Nier-type instrument (our number 2) by Dr. Sol Davison.

DESCRIPTION OF MIXTURES.—We employ the method of description found applicable to mixtures in earlier work.<sup>17</sup> The fraction of electrons in the sample associated with a particular component is called the "electron-fraction" of that component. In benzene-benzene- $d_6$  mixtures the electron fraction is practically identical with both volume and mole fraction, for the densities  $d_{25}^{25}$  of the pure components are 0.8760 and 0.9456 respectively.

# **RESULTS AND DISCUSSION**

MASS SPECTRA.—The Bureau of Standards (American Petroleum Institute) data list a total of 41 peaks below 78 in the mass spectrum of benzene. On the basis of the parent peak 78 equal to 100 the total of the other relative peak heights is 127.94 for 70 V ionizing potential. If we exclude all C<sub>6</sub> peaks, including C<sub>6</sub> itself, the total is still the rather large value of 99.69. It is very improbable that ions of carbon atom content less than 6 would reconstitute benzene in a radiation chemical process. The 100 eV yields for benzene decomposition must be of the order of the  $G(H_2)$  and  $G(C_2H_2)$  values; <sup>17</sup> i.e.  $G \simeq 0.04$ . Since, very roughly, each 100 eV input in high-energy irradiation of benzene is accompanied by formation of four ions (plus electrons), only one in 100 ions (at the most, for this calculation neglects any contribution of excited molecules) is decomposed. A straightforward conclusion consequently is that under conditions of high-energy irradiation of liquid benzene formation of ions in which only a fragment of the ring is present is much less probable than might be suggested by mass-spectral data on the attenuated gas.

In mass spectrometry, certain non-integral peaks can be used to distinguish particles of metastable ions <sup>7</sup> with half-life of the order of  $10^{-6}$  sec. Metastable ions with life  $\leq 10^{-7}$  sec are unrevealed by such spectra. In the benzene mass spectrum the only non-integral peaks reported are weak ones at 74·1, 48·1 and 34·7 and doubly charged ion peaks. There is indication of a metastable ion overlap at peak 76. A reasonable interpretation of this result in the light of the resistance of benzene to high-energy radiation is that most of the ions produced are the product of decomposition of parent ions (half-life  $\leq 10^{-7}$  sec but  $> 10^{-9}$  sec) which would be relatively stabilized in the liquid and even in the vapour state at ordinary pressures. This stabilization is presumed to occur merely by a process of collisional deactivation before the excess energy content of the ion can cause its decomposition. Such collisions would take place about every  $10^{-9}$  sec at 0·1 atm and about every  $10^{-13}$  sec in the liquid so that all that is

required is a reasonably high probability for energy transfer. In highly resonant benzene the excitation energy is distributed all over the molecule and the change in interatomic distance in any particular region is small; the configuration of the excited state is much like that of the ground state so that, given available energy states for reception of the energy, Franck-Condon restrictions on its transfer will not be great. Such transfers may occur repeatedly, the energy being d'ssipated throughout a number of molecules or ions until none contains enough energy for decomposition.

Benzene thus exhibits a kind of self-protection in radiation chemistry, in which the degree of protection is limited by availability of energy states for reception of excess excitation energy of the ions.

Comparison of mass spectra of  $C_6H_6$  and  $C_6D_6$  gives an indication of the ions stabilized before decomposition. Table 2 is based on the mass spectra of those two compounds.<sup>26</sup> The values in the table have been calculated from those data for the two isotopically pure compounds, devoid of  $C^{13}$  content. The sensitivities for appearance of the parent peaks were found to be practically identical.

Table 2.—Relative abundances of  $C_6$  ions in mass spectra of pure  $C_6H_6$  and pure  $C_6D_6$  with 70 V ionizing voltage

n	$C_6 H_n^+$	$C_6 D_{n^+}$	$C_6 H_{n^+} / C_6 D_{n^+}$
6	100.0	100.0	1.0
5	14.15	8.5	1.67
4	6·15a	3.26	1.89
3	1.47	0.86	1.71
2	4.89	2.06	2.37
1	1.61	0.66	2.44
0	0.22	0.07	3.14

<sup>*a*</sup> The Bureau of Standards data indicate that for this region normal and metastable peaks overlap. They list peak 76 only.

Table 3 compares some raw data on other ion peaks in which we have not yet corrected the values to the base of the isotopically pure ( $C^{13}$ -absent) compounds. However, the values correspond so closely to those of the true relative ion abundances that the comparisons made on this basis are nevertheless significant.

Table 3.—Uncorrected relative abundances of some selected ions in mass spectra of pure  $C_6H_6$  and pure  $C_6D_6$  with 70 V ionizing voltage. All the ions compared have relative abundance greater than 0.5

m	n	$C_m H_n^+$	$\mathbf{C}_m \mathbf{D}_n^+$	$\mathbf{C}_m \mathbf{H}_n^+ / \mathbf{C}_m \mathbf{D}_n^+$
6	6	100.0	100.0	1.0
5	3	3.28	3.4	0.96
5	2	0.71	0.63	1.3
4	4	20.2	18.5	1.1
4	3	20.08	16.7	1.2
4	2	17.42	15.65	1.1
4	1	2.92	2.43	1.2
3	2	5.68	5.15	1.1
4 3	1 2	2·92 5·68	2·43 5·15	1·2 1·1

The data of tables 2 and 3 and the well-known resistance of benzene to highenergy irradiation evoke the following train of speculation.

(i) The zero-point energy of  $C_6D_6$  carbon-hydrogen vibrations is lower than that of  $C_6H_6$  by about 1.14 kcal mole<sup>-1</sup>.<sup>27</sup>

(ii) This difference in zero-point energies is reflected in an increased resistivity of  $C_6D_6$  to high-energy radiation (see next section) and in large values of  $C_6H_n^+/C_6D_n^+$  which almost systematically increase with decrease of n. It is not reflected in the values of  $C_mH_n^+/C_mD_n^+$  shown in table 3, all of which are not greatly different from unity.

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(iii) These differences in the data for the  $C_6$  and for the other ions selected suggest a difference in mechanism by which the two groups of ions are formed. The ratio close to unity for the latter group suggests that the mechanism of formation is not very sensitive to zero-point energy. Rearrangement processes <sup>28</sup> would appear to be in this category. It is thus consistent with the facts to suggest that (except for the parent 6–6) those shown in table 3 are formed by rearrangement from the parent and those shown in table 2 are formed by successive H or D atom loss in a bond-rupture process from the parent.

(iv) The fact that G values are low in spite of the diversity and abundance of ions shown in the mass spectrometer suggests interruption of processes of formation of unstable ions, most of which originate from an ion of common formula. The latter may be formed with very high energy. We may note particularly that the relative peak heights with respect to the parents of the doubly-charged parentmolecule ions are approximately 13.6 and 14.6 for C<sub>6</sub>H<sub>6</sub><sup>2+</sup> and C<sub>6</sub>D<sub>6</sub><sup>2+</sup> respectively. Thus, we must accept as real the formation in the primary excitation of a large number of excited states (of unknown abundance) intermediate between the singly charged and the doubly charged ions. Such excited states are either deactivated by collision or decompose, as in the attenuated gas of the mass spectrometer. Even in condensed systems some small number of them may decompose to yield free atoms, radicals, or even molecules and a new ion. It is because of such processes that benzene yields product when exposed to high-energy radiation. Since more energy would be required for a C-D than for a C-H bond rupture and more time for rearrangement of a heavy molecule than of a light one, we may expect that  $C_6D_6$  would be more resistive to radiation than  $C_6H_6$ .

PRODUCTS RESULTANT FROM IRRADIATION.—Table 4 summarizes the results obtained from irradiation of benzene, benzene- $d_6$  and their mixtures with 1.5 MV electrons at 2  $\mu$ A. The original data from which these calculations were made show that the results were independent of time of irradiation and in good agreement. The values  $G(H_2) = 0.035$  and  $G(C_2H_2) = 0.020$  for pure  $C_6H_6$  are in reasonably good agreement with previously given values  ${}^{17} G(H_2) = 0.036$  and  $G(C_2H_2) = 0.022$ . In the values for "pure"  $C_6D_6$  the third significant figures given for G(hyd) = 0.0117 and G(ac) = 0.0133 are deliberately entered, particularly to emphasize the reality of the difference between the two values. We may presume with reasonable certainty that these values would be respectively practically unchanged for  $G(D_2)$  and  $G(C_2D_2)$  in isotopically pure  $C_6D_6$ .

Table 4.—Analyses and 100 eV yields of gas from mixtures of benzene and benzene- $d_6$  on irradiation with 1.5 MV electrons at 2  $\mu$ A; hyd is total hydrogen; ac is total acetylene

$C_6H_6$ ,	number of expt.	times,	C(bud)	%			$C(\alpha\alpha)$	%		
fraction	in average	min	O(liyu)	H <sub>2</sub>	HD	$\mathbf{D}_2$	(ac)	$C_2H_2$	$C_2HD$	$C_2D_2$
0.0	3a	60, 40, 40	0.0117	0.0	3.3	96.7	0.0133	0.0	1.7	98.3
0.271	1	40	0.018	30.0	34.9	35.1	0.013	35-4	8.8	55-8
0.50	3	20, 40, 60	0.020	52.1	33.1	14.8	0.014	52.3	21.1	26.1
0.766	1	40	0.026	88.6 <sup>b</sup>	6.4	5.0	0.012	80.2	7.25	12.5
1.00	4	2-60	0.035				0.020			

<sup>*a*</sup> Three analyses were rejected because of evidence of contamination of the samples in transportation. In the sample used for analysis, G values were not determined. Those given do, however, represent the average of three close results.

<sup>b</sup> Because of instrumental difficulty peak heights were uncertain by about 10 % of this analysis; analyses are thus correspondingly uncertain.

While  $G(H_2) > G(C_2H_2)$  for benzene,  $G(D_2) < G(C_2D_2)$  for benzene- $d_6$ . A reasonable conclusion is that at least two mechanisms are involved in radiolysis of benzene (i.e. both  $C_6H_6$  and  $C_6D_6$ ) and that these do not contribute in the same way to hydrogen and acetylene production.

The species HD can be formed in significant quantity only by a free radical mechanism; e.g.

$$H + C_6 D_6 \rightarrow HD + C_6 H_5$$
 (1) which competes with

$$H + C_6 H_6 \rightarrow H_2 + C_6 H_5 \tag{2}$$

or

which competes with

$$\mathbf{D} + \mathbf{C}_6 \mathbf{H}_6 \to \mathbf{H}\mathbf{D} + \mathbf{C}_6 \mathbf{H}_5 \tag{3}$$

$$\mathbf{D} + \mathbf{C}_6 \mathbf{D}_6 \to \mathbf{D}_2 + \mathbf{C}_6 \mathbf{H}_5. \tag{4}$$

Because of zero-point energy differences reaction (2) will occur more frequently than (1) and (3) will be more frequent than (4). Under such circumstances, the ratio of yields  $HD/D_2$  should much exceed the mole ratio  $C_6H_6/C_6D_{6_4}$  Table 4 shows that this situation is true except for a single case (0.766 electron fraction  $C_6H_6$ ) where there is some uncertainty about the analysis.

The activation energy differences  $E_1 - E_2$  and  $E_4 - E_3$  should be nearly the same and certainly less than the zero-point energy difference between  $C_6H_6$  and  $C_6D_6$ . No value for the difference in the range 0-1.14 kcal, however, can give the ratio  $H_2$ : HD:  $D_2$  reported for the 0.5 electron (or mole) fraction mixture if it is assumed that all  $H_2$  and  $D_2$  are formed via reactions (2) and (4). The HD yield calculated on such a basis turns out to be too high. The data are not adequate for actual calculation of  $E_1 - E_2$  ( $\simeq E_4 - E_3$ ) or of the relative amounts of free radical and ultimate molecule (i.e. rearrangement) decomposition in  $C_6H_6$  and  $C_6D_6$  but some relationships may be examined, as in table 5.

Table 5.—Estimate of sources of  $H_2$  and  $D_2$  in 0.5 mole fraction benzene + benzene- $d_6$  mixture on basis of assumptions regarding activation energy

$E_1 - E_2$ assumed, kcal/mole	HD,%			H <sub>2</sub> , %			D <sub>2</sub> , %		
	obs.	cale. from (1)	calc. from (3)	obs.	calc. from (2)	calc. rearrang.	obs.	calc. from (4)	cale. rearrang.
	33-1	20.9	12.2	52.1			14.77		
0.3					34.9	17.2		7.3	7.4
0.5					47.1	5.00		5.6	9.7

For the calculations of table 5 we assume that the relative contributions of  $C_6H_6$  and  $C_6D_6$  to the HD yield are determined by the relative probabilities of H and D formation and that these (for the 50 mole % mixture) are given by the ratio  $C_6H_5^+/C_6D_6^+ = 1.67$  in table 2. Such assumption is, at best, only approximately valid. The calculation involves the steps:

HD (from (1) calc.) = 
$$\frac{1.67}{2.67}$$
 HD (obs.),  
H<sub>2</sub> (from (2), calc.) =  $e^{(E_1 - E_2)\mathbf{R}T}$  HD (from (1), calc.),

 $H_2$  (from rearrangement, calc.) =  $H_2$  (obs.) –  $H_2$  (from (2), calc.),

similar steps for  $D_2$ , and the assumption that we may justifiably use  $T \simeq 300^{\circ}$  K. Even this latter assumption is questionable, for it ignores possible "hot-atom" effects. In spite of the limited usefulness of the results table 5 does show that if a small difference in activation energies  $E_1 - E_2 (\simeq E_4 - E_3)$  is assumed, results consistent with our knowledge can be derived. Of the two  $E_1 - E_2$  values used, the value 0.3 kcal seems nearer to the truth than 0.5 kcal because it gives lower yields of  $D_2$ , both by free-atom reaction and by rearrangement, than of  $H_2$ . The 0.5 kcal figure gives too high a value for yield of  $D_2$  by rearrangement. A smaller yield seems more probable principally on the basis of the idea that rearrangement decompositions of the heavier  $C_6H_6$  occur more slowly than those of  $C_6H_6$ —an interpretation already shown to be consistent with the data of table 3.

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The principal conclusion from table 5 is that the yields of hydrogen in the radiation chemistry of mixtures of benzene and benzene- $d_6$  are consistent with the notion of two simultaneous mechanisms, one of which yields free atoms and the other of which yields ultimate molecules in the primary act.

Fig. 1, on hydrogen G values, shows that in a mixture of  $C_6H_6$  and  $C_6D_6$ , the latter protects the former, for the H produced (either as  $H_2$  or HD) is distinctly below the value predicted merely from the electron fraction of  $C_6H_6$ . Conversely, the total D yield indicates that this protection may be at the sacrifice of  $C_6D_6$ , but the data are not conclusive on this point.

Fig. 2 on the other hand demonstrates conclusively that, so far as acetylene yields are concerned, the protection is mutual. One point for total acetylene yield is actually below the  $G(C_2D_2)$  value for pure  $C_6D_6$ .

The mechanism of acetylene production is uncertain but the existence of  $C_2HD$ yield is clear evidence that a free atom mechanism is involved. In explanation



of hydrogen from benzene) benzene- $d_6$  mixtures; hyd = total hydrogen.

of the ratio  $G(C_2H_2)/G(C_2H_4) \simeq 2$  in radiolysis of benzene vapour, Manion and Burton <sup>17</sup> suggested an explanation based on action of "hot" hydrogen atoms on the benzene molecule with two acetylene molecules and one ethylene coming from decomposition of each benzene. Ethylene is not a product of liquid radiolysis so that the mechanism must be quite different in this case. The difficulty here is that the yield of  $C_2HD$  is rather large for a conventional explanation. An explanation that fits the observations may be summed up in the following statements.

(i) In the liquid state radiolysis part of the acetylene is formed by a rearrangement mechanism and part by the action of free hydrogen atoms.

(ii) Interaction of a hydrogen atom with liquid benzene yields only one acetylene molecule.

(iii) The acetylene molecule formed by the atomic reaction contains the incident hydrogen atom. This is not the sort of process one would ordinarily imagine.

FURTHER COMMENT ON PROTECTION.-In radiation chemistry the term protection is usually applied to the protective effect of one compound by another, although the protective effect of a benzene ring on the side groups has been demonstrated. In photochemistry, the Franck-Rabinowitch effect <sup>29</sup> is a kind of protection. More inclusively defined, protection is the provision of competing means for dissipation of excitation energy prior to decomposition.<sup>30</sup> Any means which taps off energy from a potentially labile group or increases the probability of such tapping-off is a protective agent.

We have seen from consideration of mass spectrometric data that benzene may protect itself by energy-transfer of the type,

$$C_6H_6^{+*} + C_6H_6 \rightarrow C_6H_6^{+'} + C_6H_6'.$$

Similarly,

$$C_6H_6^* + C_6H_6 \rightarrow C_6H_6'' + C_6H_6'$$

The products, as a result of a series of such energy transfers, are in a potentially less labile state.

The best condition for energy transfer is to a level of exactly the same energy content. However, such a transfer is less likely to dissipate energy than the less probable transfer to a slightly different level. In the latter process some small



amount of energy is transmitted into translation. Thus, an improved arrangement for protection in such a highly resonant substance as benzene is the provision of an additional system with energy levels slightly staggered with respect to the benzene levels. Such a function may be performed by benzene- $d_6$  for benzene and by benzene for benzene- $d_6$ .

In the system benzene-benzene- $d_6$ , ionization potentials and excitation potentials are extremely close together. An explanation of protection based on those relationships is satisfactory for substances essentially different in those respects. In this case, mutual protection occurs because the two compounds act to provide for each other more effective and highly competitive processes by which energy can be transferred and dissipated before decomposition has a chance to occur.

- <sup>2</sup> Bethe, Ann. Physik, 1930, 5, 325.
- <sup>3</sup> R. R. Hentz, private communication.
- <sup>4</sup> Mohler, Bloom, Lengel and Wise, J. Amer. Chem. Soc., 1949, 71, 387.
- <sup>5</sup> Mariner and Bleakney, *Physic. Rev.*, 1947, 72, 792.
- <sup>6</sup> Langer, J. Physic. Chem., 1950, 54, 618.

<sup>&</sup>lt;sup>1</sup> cf. Viallard and Magat, *Compt. rend.*, 1949, **228**, 1118, for an excellent brief review and interpretation of some of this work.

- <sup>7</sup> cf. Hipple, J. Physic. Chem., 1948, **52**, 456; Physic. Rev., 1947, **71**, 594; Hipple, Fox and Condon, Physic. Rev., 1946, **69**, 347; Bloom, Mohler, Wise and Wells, J. Res. Nat. Bur. Stand., 1949, **43**, 65.
- <sup>8</sup> Williams, Jr. and Gevantman, J. Physic. Chem., 1952, 56 (in press).
- <sup>9</sup> cf. Berry, J. Chem. Physics, 1949, 17, 1164.
- <sup>10</sup> Sworski and Burton, J. Amer. Chem. Soc., 1951, 73, 3890.
- <sup>11</sup> cf. Burton, J. Physic. Chem., 1947, 51, 786.
- <sup>12</sup> cf. Honig, Science, 1946, 27, 104; Burton, J. Physic. Chem., 1947, 51, 611.
- <sup>13</sup> cf. particularly Breger, J. Physic. Chem., 1948, 52, 551; Burton, V. L., J. Amer. Chem. Soc., 1949, 71, 4117.
- <sup>14</sup> Burton, J. Physic. Chem., 1948, 52, 810.
- <sup>15</sup> cf. Whitehead, Goodman and Breger, J. Chim. Phys., 1951, 48, 184.
- <sup>16</sup> Hentz and Burton, J. Amer. Chem. Soc., 1951, 73, 532; Sworski, Hentz and Burton, J. Amer. Chem. Soc., 1951, 73, 1998; Burton, Gordon and Hentz, J. Chim. Phys., 1951, 48, 190.
- 17 Manion and Burton, J. Physic. Chem., 1952, 56 (in press).
- <sup>18</sup> cf. Magee and Burton, J. Amer. Chem. Soc., 1951, 73, 523; Magee, J. Physic. Chem., 1952, 56 (in press).
- <sup>19</sup> Franck-Condon restrictions, of course, apply but such restrictions are not great when the electronically excited state and the non-excited state are of approximately the same configuration. Substances like benzene, which show similar resonance both in the ground and excited states, probably offer such conditions.
- <sup>20</sup> Price, Proc. Roy. Soc. A, 1940, 174, 207.
- <sup>21</sup> Krassina, Acta Physicochim., 1939, 10, 193.
- <sup>22</sup> Zemany and Burton, J. Amer. Chem. Soc., 1951, 73, 499; J. Physic. Chem., 1951, 55, 949.
- <sup>23</sup> Ingold, Raisin and Wilson, J. Chem. Soc., 1936, 916; Best and Wilson, J. Chem. Soc., 1946, 242.
- <sup>24</sup> The heavy water used (D content 99.4 atom % of total hydrogen) was furnished by the U.S. Atomic Energy Commission.
- <sup>25</sup> Saunders and Taylor, J. Chem. Physics, 1941, 9, 616.
- <sup>26</sup> cf. Gordon and Burton, forthcoming publication, for detailed data on  $C_6D_6$ .
- <sup>27</sup> cf. Randall, Fowler, Fuson, Dangl, *Infra-red Determinations of Organic Structures* (D. Van Nostrand & Co., New York, 1949) for characteristic frequencies from which this value is calculated.
- <sup>28</sup> Rearrangement processes involve rearrangement of atoms and simultaneous change of more than one bond while the atoms of the entity involved are within molecular diameter of each other. Rupture processes involve dissociation of a bond or successive dissociation of bonds, one at a time. An atom or radical escapes in such a process before a second bond breaks.
- <sup>29</sup> Franck and Rabinowitch, Trans. Faraday Soc., 1934, 30, 120.
- <sup>30</sup> Note that protection in this sense is related to decomposition in the same way as is quenching to fluorescence.