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The γ-Radiolysis and Mercury-Photosensitized Decomposition of Ethylbenzene Vapor

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Previously we reported that, in the gas-phase radiolyses of toluene, ethylbenzene, and *m*-xylene, the benzylations of the aromatic nuclei of the parent alkylbenzene molecules were commonly observed as the main processes of the product formations.[1] These reactions have been attributed to the electrophilic substitutions by $C_7H_7^+$ ions,[2] which are well known to be the most abundant ions in the mass spectra of these alkylbenzenes.[3] Furthermore, in a preceding paper on the gas-phase radiolysis of toluene the overall product formation was studied and compared with that of the mercury-photosensitized decomposition.[4] In order to investigate the specific mode of the gas-phase radiolyses of alkylbenzenes, where ionic species and various excited molecules play important roles, we felt it was of some significance to compare those results with those of photolytic studies. In the present paper we wish to call attention to the radiolysis and mercury-photosensitized decomposition of ethylbenzene vapor at room temperature.

Experimental

The radiolysis was carried out in Pyrex cylinders approximately 120 *ml* in volume with γ-rays from a 5000 Ci cobalt-60 source. The dose rate to ethylbenzene was 4.3×10^{15} eV/hr·μmol, and the total dose, 3.1×10^{17} eV/μmol.

The photolysis of ethylbenzene containing a small amount of mercury vapor at 2537 Å was studied using cylindrical quartz cells (5 cm in diameter and 5 cm long) and a low-pressure mercury lamp.[5] The relative yields of the products were not appreciably affected by the use of a filter, Toshiba UV-25, which does not transmit below about 2000 Å; therefore, the contribution of 1849 Å light from the low-pressure mercury lamp may be neglected. The analysis of the products was the same as that described previously.[4]

Results and Discussion

Mercury-Photosensitized Decomposition. A few papers have been published on the mercury-photosensitized decomposition of ethylbenzene vapor at 2537 Å,[6,7] though these have dealt exclusively with the gaseous products. The products reported by Takase *et al.*[7] are ethane and relatively small yields of hydrogen and methane. They concluded that the major bond scission in the primary process occurs at the C–C bond β to the ring as follows:

$$\text{EB(Ethylbenzene)} \xrightarrow[\text{Hg}]{h\nu} \text{EB*} \qquad (1)$$

$$\text{EB*} \longrightarrow C_6H_5CH_2\cdot + CH_3\cdot \qquad (2)$$

and that ethane is formed almost exclusively by the combination of methyl radicals, judging from the results of the photolysis of ethylbenzene-β-d_1 vapor.

TABLE 1. THE PRODUCT YIELDS OF THE Hg-SENSITIZED PHOTOLYSIS AND γ-RADIOLYSIS OF ETHYLBENZENE VAPOR AT ROOM TEMPERATURE

Product	Photolysis μmol	Radiolysis, *G* value		
	Pressure, mmHg			
	4	4	4 with NO[b]	7.6[a]
H_2	0.046	0.71	n.d.[c]	0.76
CH_4	0.10	0.54	n.d.[c]	0.51
C_2H_2	n.d.[d]	0.46	0.50	0.56
C_2H_4	n.d.[d]	0.32	0.35	0.40
C_2H_6	0.84	0.99	0	0.92
C_3H_8	0.018	0.10	0	—
Benzene	0.022	0.41	0.28	0.38
Toluene	0.22	0.34	0.11	0.34
i-PB[e]	0.16	0.03	0	0.11
Bibenzyl	0.34	0.05	0	—
1,2-DPP[f]	0.30	0.06	0	—
2-EDPM[g]	n.d.[d]	0.06	0.06	—
3-EDPM	n.d.[d]	0.82	0.85	—
4-EDPM	n.d.[d]	0.10	0.09	—

a) Data of Wiltzbach and Kaplan (Ref. 9). The *G* values of the other products such as xylenes and ethyltoluenes are also determined.
b) The mol% of NO was 10.
c) Not determined owing to the interference with added NO.
d) Not detectable.
e) Isopropylbenzene.
f) Diphenylpropane.
g) Ethyldiphenylmethane.

The product yields of our study are presented in Table 1, together with the results of the radiolysis. The formation of large yields of the products, such as ethane and bibenzyl, which is attributable to the reactions of the radicals formed by the β C–C bond scission, the reaction (2), was also observed in our study. As is shown in Table 1, small amounts of benzene and propane,

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[1] Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

[2] The question of whether the $C_7H_7^+$ ions, which attack aromatic rings, are tropylium ions, as has been suggested in the mass-spectrometric studies (see Ref. 3), or benzyl ions still remains.

[3] H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," ed. by F. W. McLafferty, Academic Press, New York (1963), p. 453.

[4] Y. Yamamoto, S. Takamuku, and H. Sakurai, *J. Phys. Chem.*, **74**, 3325 (1970).

[5] The direct photolysis may also occur to some extent, since ethylbenzene absorbs light in the 2537 Å region.

[6] R. R. Hentz and M. Burton, *J. Amer. Chem. Soc.*, **73**, 532 (1951).

[7] A. Takase, M. Murano, H. Mikuni, and M. Takahashi, International Conference on Photochemistry, Tokyo (1965).

the latter of which is thought to be formed by the combination of methyl and ethyl radicals, were formed in almost equivalent yields; it is indicated that the scission of the α C–C bond occurs in the primary process, though to a relatively small extent.

$$EB^* \longrightarrow C_6H_5\cdot + C_2H_5\cdot \qquad (3)$$

In previous studies,6,7) the possibility of the formation of styrene has been pointed out. However, in our study styrene was not found to be produced in a detectable yield; the only primary process leading to the formation of hydrogen suggested by our results is as follows:8)

$$EB^* \longrightarrow C_6H_5\dot{C}HCH_3 + H \qquad (4)$$

In our experiment at room temperature, the predominant reactions of the radicals formed by the primary processes, (2), (3), and (4), are considered to be combinations and α hydrogen abstractions from ethylbenzene with relatively small activation energies. Thus, we can write the processes of the formation of the observed products as follows:

$$R\cdot + EB \longrightarrow RH + C_6H_5\dot{C}HCH_3 \qquad (5)$$

$$R\cdot + R\cdot \longrightarrow R\text{–}R \qquad (6)$$

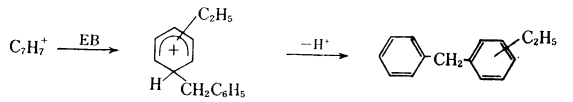
where R· represents any radical produced in the primary processes or by the hydrogen abstractions from ethylbenzene.

Neglecting the combinations of the radicals and hydrogen atoms, the yield of the $C_6H_5\dot{C}HCH_3$ radicals formed by the hydrogen abstractions (5) may be approximately represented by the sum of the yields of hydrogen, methane, benzene, and toluene. Such a yield, 0.39 μmol, was smaller than the sum of the yields of the products from $C_6H_5\dot{C}HCH_3$ radicals, isopropylbenzene (*i*-PB) and 1,2-diphenylpropane (1,2-DPP), 0.46 μmol, supporting the view that $C_6H_5\dot{C}HCH_3$ radicals are formed by the process (4) as well as by the hydrogen abstractions (5).

Radiolysis. The *G* values of the products of the gas-phase radiolysis of ethylbenzene were obtained in the presence and in the absence of a radical scavenger, nitric oxide; they are presented in Table 1, together with the results of the previous study.9) As new products which were not detected in the photolysis, acetylene, ethylene, and three isomers of ethyldiphenylmethane (EDPM) were formed in the radiolysis.

When 10 mol% NO was added, ethane, propane, *i*-PB, bibenzyl, and 1,2-DPP disappeared; it may be that these products are formed through radicals as are some benzene and toluene substances, whose yields were partially reduced by the addition of 10 mol% NO (to be discussed below). The appreciable yields of ethane and propane indicate that methyl radicals are largely formed in the primary process of the radiolysis; this is analogous with the photolysis.

The remarkable difference between the radiolysis and the photolysis was observed in the formation of dimeric products; that is, the main dimeric products in the radiolysis were EDPM's, whose yields were not appreciably affected by the addition of 10 mol% NO, while the main products in the photolysis were bibenzyl and 1,2-DPP. As has been previously reported,1) the formation of EDPM's may be attributed to the ion-molecule reaction of the $C_7H_7^+$ ions with ethylbenzene, as is shown by the following scheme:10)



On the basis of these results, it may be concluded that the major bond scission in the primary process of the gas-phase radiolysis of ethylbenzene occurs at the β C–C bond *via* ionization, resulting in the formation of a methyl radical and the $C_7H_7^+$ ion as follows:

$$EB \rightsquigarrow EB^{+*} \qquad (7)$$

$$EB^{+*} \longrightarrow C_7H_7^+ + CH_3\cdot \qquad (8)$$

The formation of the $C_7H_7^+$ ions is the most important process observed in the mass spectrometry of ethylbenzene as well as in those of toluene and xylenes.3)

When 10 mol% of NO was added, ethylene and acetylene were not appreciably affected, indicating that these products are formed through intermediates unscavengeable with NO. In our study of the gas-phase radiolysis of toluene,4) the yield of ethylene was negligible over the pressure range studied (2 to 19 mmHg); the fact that the *G* value of ethylene from ethylbenzene is much larger than that from toluene seems to indicate that a great portion of ethylene is formed from the side chain, the ethyl group, of ethylbenzene, probably through an excited ethyl radical.11) On the other hand, the *G* value of acetylene from ethylbenzene was of the almost same order as that from toluene; the processes of the acetylene formation suggested in the gas-phase radiolysis of toluene,4) that is, the fragmentations of the $C_7H_7^+$ ions and aromatic rings, is probable for the ethylbenzene radiolysis.

The dependence of the yields of benzene and toluene on the NO concentration was studied. These yields were partially reduced by the addition of 10 mol% NO (Table 1); it was also observed that both were almost constant above about 6 mol% NO, indicating the presence of the unscavengeable benzene and toluene. The mechanism of the formation of these unscavengeable products is uncertain, though the possible mechanisms might be thought to involve the reactions of $C_6H_5^+$ ions12) and $C_7H_7^+$ ions.

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8) The dissociation of this bond might also occur by means of the reaction of the excited mercury atoms and ethylbenzene molecules.

9) K.E. Wiltzbach and L. Kaplan, *Advances in Chemistry Series*, No. 82, American Chemical Society, Washington, D. C., (1968), p. 134.

10) In a previous paper (Ref. 1), the isomer distribution of EDPM's has been accounted for by the isomerization of the intermediate complexes, $C_{15}H_{17}^+$ ions; the precise mechanism of such an electrophilic substitution of aromatic rings by $C_7H_7^+$ ions has also been discussed in a previous paper on the gas-phase radiolysis of toluene (Ref. 4).

11) The formation of ethylene by the decomposition of the excited ethyl radicals has been proposed in the vacuum ultraviolet photolysis of saturated hydrocarbons [J. R. McNesby and H. Okabe, "Advances in Photochemistry," Vol. 3, ed. by W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y. (1964), p. 204].

12) The $C_6H_5^+$ ions are the product ions in the mass spectra of toluene and ethylbenzene (see Ref. 3); the formation of unscavengeable benzene was also observed in the gas-phase radiolysis of toluene (see Ref. 4).

The most interesting result obtained in these experiments was that the β bond scissions are the major primary process in both the γ-radiolysis and the mercury-photosensitized decomposition of ethylbenzene vapor. However, in the former, the $C_7H_7^+$ ions result, while the latter results in benzyl radicals. A similar result was also obtained in the study of toluene vapor, as has previously been reported.4)