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Structure and Reactivity of Organic Ions in Gas-Phase Radiolysis. III. The Benzenonium Ions Formed by the Reactions of CH_5^+ and $C_2H_5^+$ Ions from Methane with *o*-Xylene[1]

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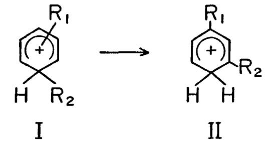
The gas-phase radiolysis of mixtures of *o*-xylene and excess methane has been studied at room temperature as a function of methane pressure and the added NO and NH_3 in order to investigate the reactions of CH_5^+ and $C_2H_5^+$ ions from methane with *o*-xylene. It has been suggested that the proton transfers from these ions to *o*-xylene result in the isomerization to *m*-xylene *via* an intermediate σ complex, dimethylbenzenonium ion, and that a part of the $C_2H_5^+$ ions is added to *o*-xylene leading to the formation of two isomers of dimethylethylbenzene. The proposed mechanism of the methane-sensitized isomerization of *o*-xylene to *meta* isomer has been supported by the observation that both *m*-xylene-d_0 and *m*-xylene-d_1 were formed in the radiolysis of a mixture of *o*-xylene and methane-d_4. The isotope effect (k_H/k_D) on the proton loss from the dimethylbenzenonium ion was roughly estimated to be 1.8 ± 0.4. Group migration of intermediate σ complexes was discussed.

In previous studies,[2–5] it was reported that, in the gas-phase radiolysis of toluene, ethylbenzene, and *m*-xylene, $C_7H_7^+$ ions,[6] formed from these alkylbenzenes, react with the parent alkylbenzene molecules to produce the corresponding benzylated alkylbenzenes, alkyldiphenylmethanes.[7] The products predominantly consisted of such isomers as are benzylated at a *meta* position to the resident alkyl groups. It has also been reported that, in the gas-phase radiolysis of a mixture of propane with benzene or toluene, the isopropylation of the aromatics by $C_3H_7^+$ ions from propane was observed, and in the case of toluene the isopropylation occurred mainly at a *meta* position at higher pressures of toluene.[1] Attention was paid to the mechanism of these electrophilic aromatic substitution reactions in the gas phase in order to explain the observed isomer distribution of the products, which is in contrast to that known in analogous liquid-phase reactions such as the Friedel-Crafts reactions.[8] We have proposed a mechanism involving an isomerization process of intermediate σ complexes, benzenonium ions,[1,3] where R_1 and R_2 show the resident and attacking alkyl groups, respectively.



Thus, it has been suggested that the primarily formed complex I easily isomerizes to the more stable one II, which is most effectively stabilized by the inductive effect of alkyl groups, since in the gas phase it exists as a free ion with a certain internal energy. We have extended the study of this type of reaction, which proceeds through benzenonium ion intermediate, especially in order to investigate its intramolecular rearrangement.

In the high pressure mass spectrometry of methane, it has been reported that the major product ions at higher pressures are CH_5^+ and $C_2H_5^+$ ions, which comprise approximately 90% of the total ionization.[9] The ions are unreactive with methane but highly reactive with some kinds of additives such as ammonia, water, and aromatic hydrocarbons.[10,11] Munson and Field reported that these ions react with several aromatic hydrocarbons to yield predominantly protonated aromatic ions along with a relatively small amount of ethyl ion adducts.[11] The present investigation deals with the reactions of these benzenonium ions expected to

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[1] Part II; S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, **93**, 2420 (1971).

[2] Y. Yamamoto, S. Takamuku, and H. Sakurai, *ibid.*, **91**, 7192 (1969).

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

[4] Y. Yamamoto, S. Takamuku, and H. Sakurai, This Bulletin, **44**, 574 (1971).

[5] Y. Yamamoto, S. Takamuku, and H. Sakurai, *ibid.*, **44**, 2104 (1971).

[6] This ion is known to be the most abundant ion in the mass spectra of toluene, ethylbenzene, and xylenes (see Ref. 17).

[7] The analogous product formation was observed in the gas-phase radiolyses of *o*- and *p*-xylenes, and the results will be published.

[8] See for example, C. C. Price, "Organic Reactions," Vol. 3, John Wiley & Sons, Inc., New York, N. Y. (1964), p. 1.

[9] F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 3289 (1965).

[10] M. S. B. Munson and F. H. Field, *ibid.*, **87**, 4242 (1965).

[11] M. S. B. Munson and F. H. Field, *ibid.*, **89**, 1047 (1967).

be also formed in the gas-phase radiolysis of mixtures of *o*-xylene and excess methane.

Experimental

Materials. *o*-Xylene obtained from Wako Pure Chem. Indust. Co. was purified by the usual method. After distillation using a 1 m column packed with stainless helices, the purity determined gas chromatographically by means of flame-ionization detection was more than 99.9%. The purified *o*-xylene was dried over sodium, degassed, and stored in a high vacuum line. Methane-h_4 and methane-d_4, obtained from Takachiho Shoji Co. and Merck and Dohme of Canada, respectively, were also stored in the vacuum line, after several trap-to-trap distillations. These samples were thoroughly dried by passing through sodium mirrors prior to use. Ammonia and nitric oxide, both obtained from Takachiho Shoji Co., were also purified by several trap-to-trap distillations.

Procedures. Experimental procedures were almost the same as those reported previously.1) Irradiation was carried out in Pyrex cylinders approximately 120 m*l* in volume with γ rays from a 5000 Ci ^{60}Co source at room temperature. The dose rate and the dose were 3.7×10^{15} eV/hr·μmol and 2.6×10^{17} eV/μmol, respectively, for *o*-xylene. The products were analyzed by gas chromatography using a combination of Bentone 34 (3 m) and Apiezon L (3 m) and a flame-ionization detector. The column temperatures were 100 and 140°C for the products with retention times less and more than that of *o*-xylene, respectively. The isotopic distribution of *m*-xylene formed in the radiolysis of a mixture of *o*-xylene and methane-d_4 was determined using a directly coupled gas chromatograph-mass spectrometer (Hitachi RMS-4 mass spectrometer) at an ionizing potential of 80 eV.

Results and Discussion

All the radiolysis experiments were performed at the same pressure of *o*-xylene, 3.3±0.2 mmHg. The *G* values were calculated on the basis of the energy absorbed by *o*-xylene. The *G* values of the products of the gas-phase radiolysis of a mixture of *o*-xylene and methane in the presence and absence of a radical scavenger, nitric oxide, together with those of the radiolysis of pure *o*-xylene are presented in Table 1.12) The dependence of the product yields on methane pressure is shown in Figs. 1 and 2. When excess methane was added to *o*-xylene, the *G* values of *m*-xylene, *o*-ethyltoluene, and 1,2,3- and 1,2,4-trimethylbenzenes appreciably increased, and 1,2-dimethyl-3-ethylbenzene and 1,2-dimethyl-4-ethylbenzene were newly formed. The yields of these products increased with increasing methane pressure. Among these products, *o*-ethyltoluene and two isomers of trimethylbenzene were appreciably reduced by the addition of NO (Table 1). Thus, it is suggested that these products are mainly formed by the reactions of radicals from methane with *o*-xylene as follows.

Table 1. The *G* values of products in gas-phase radiolyses of pure *o*-xylene and *o*-xylene-methane mixture

Product	Pure *o*-xylene	*o*-Xylene-methane mixture *o*-Xylene, 3.3 mmHg Methane, 51.0 mmHg	
			with NO$^{a)}$
Benzene	0.14	0.07	0.08
Toluene	0.44	0.55	0.34
Ethylbenzene	0.02	0.05	0.02
p-Xylene	0.07	0.11	0.11
m-Xylene	0.19	0.73	0.61
o-Ethyltoluene	0.14	0.66	0.01
1,2,3-Trimethylbenzene	0.06	0.40	0.07
1,2,4-Trimethylbenzene	0.04	0.33	0.14
1,2-Dimethyl-3-ethylbenzene	0	0.40	0.51
1,2-Dimethyl-4-ethylbenzene	0	1.03	1.18

a) The mol ratio of added NO to methane was about 0.07.

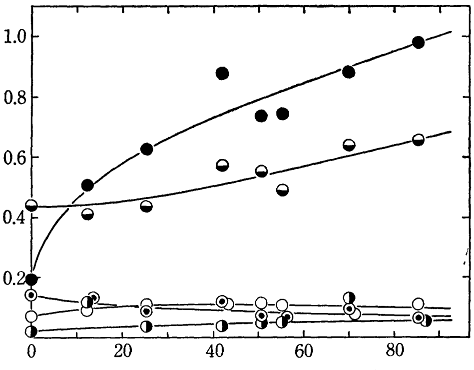

Fig. 1. Dependence of the *G* values on methane pressure (1): ⊙, Benzene; ◒, Toluene; ◑, Ethylbenzene; ○, *p*-Xylene; ●, *m*-Xylene.

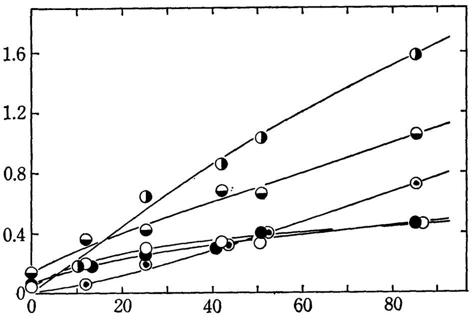

Fig. 2. Dependence of the *G* values on methane pressure (2): ◒, *o*-Ethyltoluene; ●, 1,2,3-Trimethylbenzene; ○, 1,2,4-Trimethylbenzene; ⊙, 1,2-Dimethyl-3-ethyl-benzene; ◑, 1,2-Dimethyl-4-ethylbenzene.

$$\mathrm{R\cdot + (CH_3)_2C_6H_4 \longrightarrow RH + CH_3C_6H_4CH_2\cdot} \qquad (1)$$

$$\mathrm{CH_3C_6H_4CH_2\cdot + CH_3\cdot \longrightarrow CH_3C_6H_4CH_2CH_3} \qquad (2)$$

$$\mathrm{CH_3\cdot + (CH_3)_2C_6H_4 \longrightarrow (CH_3)_3C_6H_3 + H} \qquad (3)$$

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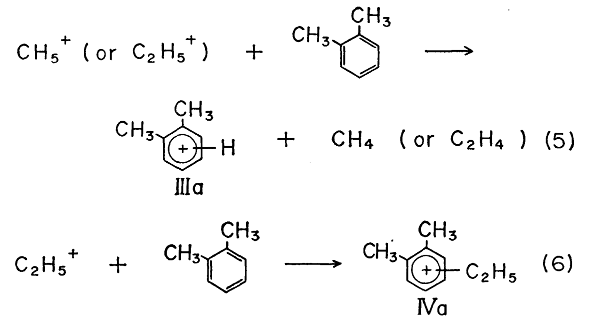
12) In a previous study of the gas-phase radiolysis of pure *o*-xylene, it was reported that benzocyclobutene is also formed with a *G* value of 0.08 at a *o*-xylene pressure of 4.7 mmHg [K. E. Wilzbach and L. Kaplan, *Advances in Chemistry Series*, No. 82, American Chemical Society, Washington, D. C., (1968), p. 134]. However, the yield of this product could not be determined under the analytical conditions of this study. The yields of other liquid products in these studies are in good agreement with each other.

where R· shows any radical or a hydrogen atom formed from methane. On the other hand, *m*-xylene and two isomers of dimethylethylbenzene were not so much affected by the added NO, indicating that the methane-sensitized isomerization and ethylation of *o*-xylene are nonradical processes.

It might be expected that the major ionic reactions in the primary process of the gas-phase radiolysis of mixtures of *o*-xylene and excess methane are the proton transfer from the CH_5^+ and $C_2H_5^+$ ions and the addition of the $C_2H_5^+$ ions to *o*-xylene as follows.

$$CH_4 \rightsquigarrow CH_5^+,\ C_2H_5^+ \qquad (4)$$



In solution chemistry it is known that the acid-catalyzed isomerization of *o*-xylene results in the exclusive formation of *m*-xylene.[13] Such a result is similar to that of the methane-sensitized isomerization of *o*-xylene. Thus, the methane-sensitized isomerization might be attributed to an acid-catalyzed reaction where the CH_5^+ and $C_2H_5^+$ ions act as Brφnsted acids to *o*-xylene. Ethylation of *o*-xylene might also be considered to be an electrophilic substitution reaction by the $C_2H_5^+$ ions analogous to the benzylation and isopropylation of aromatics.[1-5]

It has been reported that the CH_5^+ and $C_2H_5^+$ ions from methane are highly reactive with NH_3 though unreactive with NO[10]

$$CH_5^+ \text{ (or } C_2H_5^+\text{)} + NH_3 \longrightarrow NH_4^+ + CH_4 \text{ (or } C_2H_4\text{)} \qquad (7)$$

Thus, it may be expected that a competition would occur between reactions (5) and (6) and reaction (7) in the *o*-xylene-methane-NH_3 system. The effect of added NH_3 on the yields of *m*-xylene and two isomers of dimethylethylbenzene was studied from this point of view at a methane pressure of 51.1 mmHg, and the result is shown in Fig. 3. It was observed that the *G* values of these products decreased apparently with increasing NH_3 concentration, while those of *o*-ethyltoluene and two isomers of trimethylbenzene, formed by radical reactions, were not appreciably affected by the added NH_3. Thus, it seems reasonable to conclude that the methane-sensitized isomerization and ethylation of *o*-xylene are initiated by reactions (5) and (6), respectively, and the subsequent reactions may be considered to be as follows.

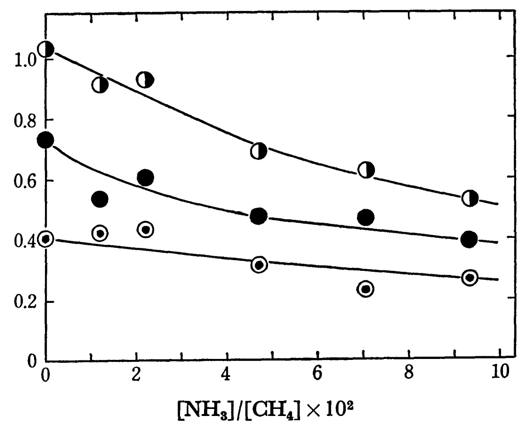
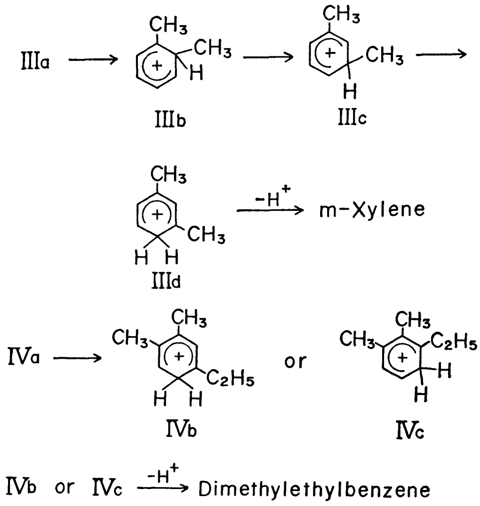


Fig. 3. Effect of added NH_3: ●, *m*-Xylene; ⊙, 1,2-Dimethyl-3-ethylbenzene; ◑, 1,2-Dimethyl-4-ethylbenzene.



where the primarily formed intermediate σ complexes IIIa and IVa have certain excess internal energies because of the exothermicities of reactions (5) and (6), and are easily isomerized to the more stable σ complexes IIId and IVb or IVc, respectively. The mechanisms are identical with those of the acid-catalyzed isomerization of *o*-xylene in solution and of the benzylation and isopropylation of aromatics in gas-phase radiolysis.[1,3] The loss of a proton from the intermediate σ complexes to produce the neutral products may be considered to be due to the proton transfer from these complexes to *o*-xylene molecules or to other species with higher proton affinities existing in the radiolytic system.[1,3]

As is shown in Figs. 1 and 2, the dependence of the *m*-xylene yield on methane pressure differed from those of two isomers of dimethylethylbenzene; the sensitization effect on the formation of *m*-xylene was appreciably reduced at higher pressures of methane, while the yields of dimethylethylbenzenes increased almost linearly with methane pressure. Such a deviation of the plot of the *m*-xylene yield against methane pressure from linearity could be explained by a selective consumption of the CH_5^+ ions by the radiolysis products from methane; it has been reported that in the high pressure mass spectrometry of methane containing a small amount of ethane, which is the most abundant hydrocarbon product in the gas-phase radiolysis of methane,[14] the

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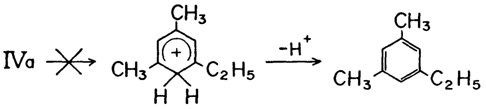
[13] H. C. Brown and H. Jungk, *J. Amer. Chem. Soc.*, **77**, 5579 (1955).

[14] See for example, K. Yang and P. J. Manno, *ibid.*, **81**, 3507 (1959).

CH_5^+ ions rapidly decrease with increasing pressure, while the $C_2H_5^+$ ions somewhat increase.[15]

The activation energy of the acid-catalyzed isomerization of *o*-xylene in solution has been estimated to be 22.8 kcal/mol;[13] it may be considered that the analogous reaction in the gas phase requires the same order of activation energy. The reaction heats of the protonation of benzene by the CH_5^+ and $C_2H_5^+$ ions have been calculated to be −32 and +3 kcal/mol, respectively,[11] although those for *o*-xylene are not known. Since the methyl inductive effect would result in a higher proton affinity of *o*-xylene than that of benzene, the protonation of *o*-xylene by the CH_5^+ ion may be considered to be exothermic with more than 32 kcal/mol. Thus, it seems also correct to conclude that the protonation of *o*-xylene by the CH_5^+ ions results in the isomerization to *m*-xylene; the overall reaction is exothermic. However, it is not at present possible to decide whether the $C_2H_5^+$ ions contribute to the isomerization of *o*-xylene as well as the CH_5^+ ions or not.

In these experiments of the gas-phase radiolysis of mixtures of *o*-xylene and methane, 1,3-dimethyl-5-ethylbenzene was not detected. This indicates that the migration of the resident methyl groups of *o*-xylene does not occur in the transition state of the ethylation of *o*-xylene by the $C_2H_5^+$ ions, in spite of the fact that it gives the most stable σ complex of the dimethylethylbenzenonium ions as follows.



This finding could probably be explained in terms of the activation energy of the methyl migration and the excess internal energy of the intermediate complex IVa.

In order to obtain further information about the mechanism of the methane-sensitized isomerization in gas-phase radiolysis, the radiolysis of a mixture of *o*-xylene and methane-d_4 was examined at a methane-d_4 pressure of 51.4 mmHg, and the mass spectrum of the produced *m*-xylene was measured and compared with that of authentic *m*-xylene-d_0, both of which are shown in Fig. 4. The *G* value of *m*-xylene in this experiment was 0.81, and no difference in the product formation was observed between the experiments using methane-d_0 and methane-d_4. The mass spectra shown in Fig. 4 indicate that both *m*-xylene-d_1 and *m*-xylene-d_0 were formed in the radiolysis of the mixture of *o*-xylene and methane-d_4.[16] The mechanism proposed above is supported by this result; the deuterium ion transfer from the CD_5^+ and $C_2D_5^+$ ions to *o*-xylene yields the benzenonium ion containing a deuterium atom which, after the methyl migration, loses a proton or a deuterium ion to give *m*-xylene-d_1 or *m*-xylene-d_0, respectively. The ratio of *m*-xylene-d_1 to *m*-xylene-d_0 was calculated to be 2.0±0.2 from the relative intensities of the ions with mass 91, 92, and 93 of these mass spectra. The calculation was based on the assumption that the *m*-xylene-d_1, which contains the deuterium in the aromatic ring, yields the mass 91 and 92 ions with the relative yields of 11 and 89%, respectively.[17] An estimation of the isotope effect (k_H/k_D) on the proton loss from the intermediate σ complex IIId is possible on the basis of the following assumptions: (a) In the radiolysis of the mixture of *o*-xylene and methane-d_4, *m*-xylene is formed by the direct energy absorption of *o*-xylene with the same *G* value as in the direct radiolysis of *o*-xylene, 0.19 (Table 1). (b) The increase of *m*-xylene by the addition of methane-d_4 to *o*-xylene is exclusively attributed to the reactions of the CD_5^+ and $C_2D_5^+$ ions with *o*-xylene. (c) In the transition state of the methane-sensitized isomerization of *o*-xylene, a rapid hydrogen migration occurs around a ring of the intermediate σ complex, and the deuterium is statistically distributed among the five possible positions attached to the ring carbons before the loss of a proton or a deuterium ion.[18] The value of k_H/k_D obtained in this way was 1.8±0.4.

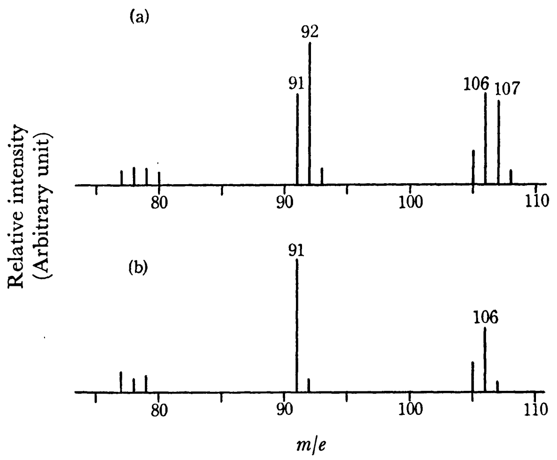


Fig. 4. Partial mass spectra of (a) the *m*-xylene formed in the gas-phase radiolysis of an *o*-xylene-CD_4 mixture and (b) authentic *m*-xylene-d_0.

The most interesting result obtained in this study is that the ionic species formed from methane by γ irradiations react with *o*-xylene to produce *m*-xylene *via* an intermediate σ complex, and this reaction is identical with the acid-catalyzed isomerization of *o*-xylene in solution. This conclusion was strongly supported by the isotopic distribution of the *m*-xylene, formed in the gas-phase radiolysis of a mixture of *o*-xylene and methane-d_4.

We wish to thank Mr. Tamotsu Yamamoto and Mr. Tomikazu Sawai in the Radiation Laboratory for assistance in the γ irradiations.

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[15] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965).

[16] The mass spectra indicate that no other *m*-xylene containing more than one deuterium atom was formed; the *m*-xylene-d_1 was not formed by a hydrogen-deuterium exchange reaction on the produced *m*-xylene-d_0.

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

[18] This assumption seems to be reasonable on the basis of the following reports: a) Rapid hydrogen migration around the ring of benzenonium ions has been observed in acidic solutions of aromatic hydrocarbons. See for example, G. A. Olah, R. H. Schlosberg, D. P. Kelly, and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970). b) In the high pressure mass spectrometry of methane containing a small amount of 1-methyl-4-isopropylbenzene, the result has been accounted for by rapid hydrogen migration (see Ref. 11).