The Structure and Reactivity of Organic Ions in Gas-phase Radiolysis. VIII. The $C_7H_7^+$ Ion from Toluene and Ethylbenzene

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The gas-phase radiolysis of a mixture of toluene or ethylbenzene and dimethylamine has been studied at room temperature as a function of the dimethylamine pressure in order to investigate the structure and reactivity of the $C_7H_7^+$ ion. The structure of the $C_7H_7^+$ ion which takes part in the subsequent ion-molecule reaction was suggested to be the benzyl type on the basis of the reaction products. The radiolyses of toluene-α-d_3 and ethylbenzene-α-d_2 in the presence and in the absence of dimethylamine have been investigated, and the following information has been obtained: (i) the $C_7H_7^+$ ion formed from toluene and ethylbenzene mainly consists of the benzyl ion, retaining its original structure; (ii) two types of scrambling processes may be involved in the $C_7H_7^+$ ion formation, one of which, especially important in the case of toluene, includes the ring expansion of the original molecular ion, while the other consists of repeated rapid isomerization between the benzyl ion and the tropylium ion. These results were compared with those of mass spectrometric studies, which indicate that an almost complete isotope scrambling occurs, hence supporting the symmetrical tropylium structure for the $C_7H_7^+$ ion.

The structure of the $C_7H_7^+$ ion formed by the electron impact of toluene and higher alkylbenzenes has been the subject of numerous mass spectrometric investigations.[1)] Extensive labeling experiments indicate the $C_7H_7^+$ ion, which further decomposes to the $C_5H_5^+$ ion, is a symetrical tropylium ion rather than a benzyl ion.[2)] For example, the isotope retentions in the $C_7H_7^+$ ions from deuterated toluenes indicate that the eight hydrogen atoms are almost completely scrambled in the molecular ion. On the basis of this evidence and energetic considerations, Meyerson concluded that the toluene molecular ion rearranges to a cycloheptatriene-like structure of an even higher symmetry.[3)] Harrison proposed instead an irreversible isomerization of the molecular ion to the cycloheptatriene isomer involving a transfer of an α-hydrogen to the adjacent ring carbon atom, followed by the insertion of the methylene group at random between any two ring carbon atoms.[4)] This random insertion, leading to carbon scrambling, has been supported by studies using di-^{13}C-labeled toluene.[5),6)]

Furthermore, Harrison's postulation has been supported by Howe and McLafferty.[7)] They have also reported that the degree of scrambling decreases with an increase in the internal energy; hence, in the case of toluene some part of the $C_7H_7^+$ ion is formed by the direct dissociation of α-hydrogen before the scrambling of the hydrogen atoms occurs. For ethylbenzene, the tropylium structure has been again assigned to the $C_7H_7^+$ ion, although the formation process has not been clarified.[2)]

More recently, Dunbar[8)] has investigated the photoexcitation of toluene parent ions by ion-cyclotron resonance and shown that the photodissociation occurs with a complete hydrogen scrambling and a strong isotope effect. The energy dependence agrees with that determined for dissociative electron-impact ionization by Howe and McLafferty.[7)] However, it has been also shown that non-dissociating $C_7H_8^+$ ions from toluene and cycloheptatriene are non-interconverting and that there is no important degree of interconversion among the toluene, cycloheptatriene, and norbornadiene molecular ions or conversion to a common structure, as determined on the basis of different photodissociation curves of these compounds.[9)] This behavior is also in accord with the conclusion drawn from the ion-molecule reaction of $C_7H_8^+$ ions with nitrate by Hoffman and Bursey.[10)]

On the other hand, during the course of our investigations of the gas-phase radiolysis it has been found that the $C_7H_7^+$ ions from toluene, ethylbenzene, xylenes, and cycloheptatriene react with aromatics to produce benzylated compounds; the reaction has been regarded as an electrophilic substitution reaction, which is well-known in solution chemistry.[11),12)] Such a reactivity of the $C_7H_7^+$ ion with aromatics, as well as the structures of the products, seemed to suggest that the $C_7H_7^+$ formed in the gas-phase radiolysis of these compounds is a benzyl ion with a positive-charged center rather than a tropylium ion in which the positive charge is distributed equally among the seven carbon atoms. However, the question has been raised whether a tropylium ion is produced, since such a less electrophilic ion can hardly react with aromatics even if formed.

In connection with these problems, we have investigated the gas-phase radiolysis of alkylbenzene–dimethylamine (DMA) mixture. DMA has a higher basicity than aromatics and, therefore, would be expected to react with the tropylium ion.[13)] Moreover, we have also investigated the gas-phase radiolysis of toluene-α-d_3 and ethylbenzene-α-d_2 in order to obtain information about the formation process of the $C_7H_7^+$ ion. The present paper will describe the structure and formation process of the ion from toluene and ethylbenzene on the basis of more evidence than in the preceding communications.[14)]

Experimental

Materials. Toluene and ethylbenzene obtained from the Wako Pure Chemicals Industries Co. were fractionated through a spinning-band column after the usual purification. The purity, as determined gas-chromatographically, was more than 99.9%. The xylene isomers were purified in the same way; the purities were more than 99.1%. Cycloheptatriene prepared by the pyrolysis of 7,7-dichloronorcarane was purified by preparative gas chromatography. Norbornadiene obtained from the Aldrich Chemical Company, Inc. was purified by preparative gas chromatography. The DMA was evolved by heating an aqueous dimethylamine solution obtained from the Wako Pure Chemicals Industries Co., dried by being passed through a KOH column twice, and stored in a storage bulb. Oxygen obtained from the Awao Industrial Co. was dried by means of a P_2O_5 column and was then used without further purification.

The toluene-α-d_3 was prepared by the method given in the literature,[15] and the deuterium content of the methyl group was determined to be more than 93.5% by NMR analysis. Ethylbenzene-α-d_2 was prepared by means of the following paths:

$$C_6H_5COCH_3 \xrightarrow{LiAlD_4} C_6H_5CD(OH)CH_3 \xrightarrow{SOCl_2}$$

$$C_6H_5CDClCH_3 \xrightarrow{LiAlD_4} C_6H_5CD_2CH_3$$

The isotopic purity was found by NMR analysis to be better than 99%. *N*,*N*-Dimethylbenzylamine-α-d_2, a standard authentic sample for analytical purposes, was prepared by the reduction of *N*,*N*-dimethylbenzamide with $LiAlD_4$ under THF reflux conditions. The isotopic purity was found to be better than 99% by NMR analysis.

Procedures. The experimental procedures were almost the same as those reported previously[11b] With the exception of the labeled experiments, all the irradiations were carried out in Pyrex cylinders approximately 110 ml in volume with γ-rays from a 5000 Ci ^{60}Co source at room temperature. The dosimetry was based on $G(C_2H_4 \rightarrow H_2) = 1.28$,[16] assuming that the energy distribution was proportional to the electron density of the sample. The dose rates in the present experiments were 3.0×10^{15} eV/hr·μmol for toluene, cycloheptatriene, and norbornadiene, and 3.47×10^{15} eV/hr·μmol for ethylbenzene and xylenes. The *G*-values in the runs were calculated on the basis of the energy absorbed by alkylbenzene, cycloheptatriene, or norbornadiene alone. The identification of the products was carried out by gas–chromatographic comparison with authentic samples using several columns (Apieson L—KOH, 6 m at 80 °C or 140 °C and Amine 3 m at 80 °C).[17] The yields of the products were determined by a comparison of the peak areas with those of known amounts of benzene, which were submitted to gas chromatography before each analysis. The calibration of the sensitivity for a flame-ionization detector was also carried out.

For the labeled experiments, spherical cells approximately 5 l in volume were used. Irradiation was carried out with a 3000 or 7000-Ci ^{60}Co source. The irradiated samples were collected in a glass tube by trap distillation. The reaction products, *N*,*N*-dimethylbenzylamine or diphenylmethanes, were isolated by preparative gas chromatography (Apiezon L–KOH, 3 m at 105 °C and Thermol 2 m at 190 °C respectively). The product isolated in a trap was dissolved with CCl_4 for NMR measurements and then submitted to NMR spectrometry (Hitachi Perkin-Elmer R-20 spectrometer), using CAT and a gas chromatography-mass spectrometry combination (Hitachi RMS-4).

Results and Discussion

The Reaction of the $C_7H_7^+$ Ion with DMA. Toluene-DMA mixtures were irradiated with ^{60}Co γ-rays to a dose of 8.4×10^{18} eV at 10 mmHg of toluene at room temperature. The formation of *N*,*N*-dimethylbenzylamine (DMBA) and a trace amount of an unknown product were observed, along with such products as benzene, ethylbenzene, xylenes, bibenzyl, and methyldiphenylmethanes(MDPM), which are known as radiolysis products of toluene. Figure 1 shows the correlation between the yields of DMBA and MDPM from toluene irradiated in the presence of varying amounts of DMA. The yields of these products were not affected by oxygen added as a radical scavenger. Quite similar relationships between DMBA and ethyldiphenylmethanes (EDPM) were also observed in the radiolysis of ethylbenzene–DMA mixtures, as is shown in Fig. 2. In this case, the formation of a small amount of *N*,*N*-dimethyl-α-phenethylamine was observed in addition to that of DMBA. Furthermore, in the radiolysis of xylenes, cycloheptatriene, and norbornadiene in the presence of DMA, the formation of DMBA was observed and the yields were not affected by the addition of oxygen (Table 1). These hydrocarbons are known to produce a similar $C_7H_7^+$ ion by electron impact.[18,19] Thus, the results suggest the formation of a common $C_7H_7^+$ ion as a precursor of both alkyldiphenylmethanes and DMBA, as is shown in Eqs.(1)—(3).

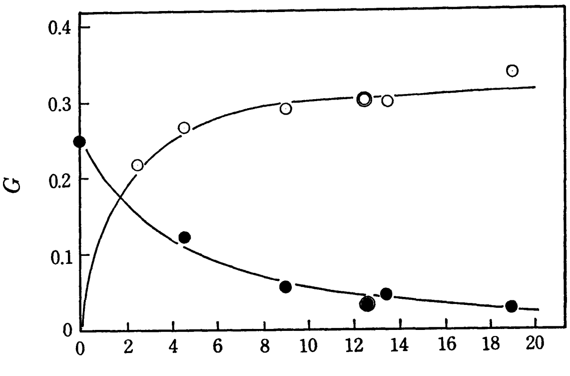


Fig. 1. Variations of the yields of methyldiphenylmethanes (MDPM, ●) and *N*,*N*-dimethylbenzylamine (DMBA, ○) as a function of the dimethylamine pressure in the radiolysis of toluene vapor (10 mm); ◉, ◎, when 10 mol% of oxygen was added.

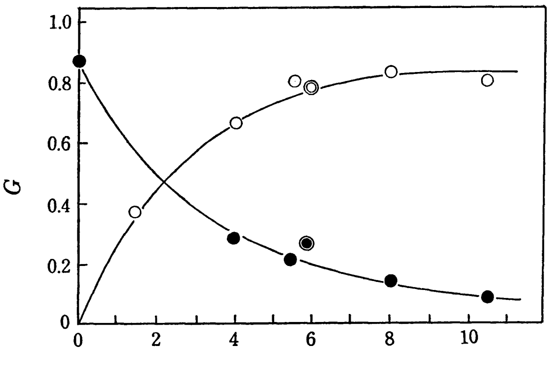
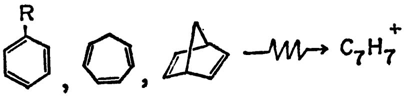


Fig. 2. Variations of the yields of ethyldiphenylmethanes (EDPM, ●) and *N*,*N*-dimethylbenzylamine (DMBA, ○) as a function of the dimethylamine pressure in the radiolysis of ethylbenzene vapor (4 mm); ◉, ◎, when 10 mol% of oxygen was added.



(1)

Table 1. The yields of DMBA produced in the gas-phase radiolysis of hydrocarbon-dimethylamine mixtures

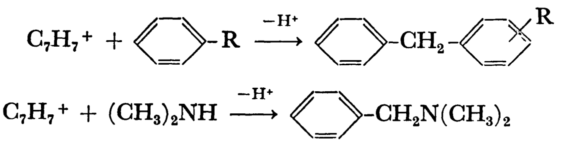
Hydrocarbon	Pressure, mmHg	Dimethylamine, mmHg	G(DMBA)	G(DMBA) with O_2[a]
Toluene	10	13.5	0.30	0.30
Ethylbenzene	4	5.5	0.82	0.78
o-Xylene	4	6	0.24	0.26
m-Xylene	4	6	0.21	0.22
p-Xylene	4	6	0.23	0.25
Cycloheptatriene	10	14	0.19	0.26
Norbornadiene	11	14	0.22	0.21

a) Oxygen was added up to about 10 mol%.

Table 2. The NMR data of D-labeled products in the radiolysis of ethylbenzene-α-d_2 and toluene-α-d_3.

Reactant (mmHg)	Product	H_{CH_2}/H_{Ph}[a] Calculated (Complete scrambling)	H_{CH_2}/H_{Ph}[a] Observed	Scrambling (%)
Ethylbenzene-α-d_2(2.2)-DMA(3.8)	DMBA	0.40	0	0
Ethylbenzene-α-d_2(1.0)-DMA(1.7)	DMBA	0.40	0.084	27.2
Ethylbenzene-α-d_2(5)	EDPM	0.189	0.024	14.5
Ethylbenzene-α-d_3(3)	EDPM	0.189	0.028	17.4
Ethylbenzene-α-d_3(1)	EDPM	0.189	0.045	27.1
Ethylbenzene-α-d_3(0.4)	EDPM	0.189	0.063	37.5
Toluene-α-d_3(8)-DMA(12)	DMBA	0.40	0.14	36~39
Toluene-α-d_3(19)	MDPM	0.24	0.062	31~33

a) DMBA, H_{Ph}, τ 2.7—2.9, H_{CH_2}, τ 6.6; MDPM, H_{Ph}, τ 2.9—3.1, H_{CH_2}, τ 6.1; EDPM, H_{Ph}, τ 2.7—3.1, H_{CH_2}, τ 6.1



(2)

(3)

From the data shown in Figs. 1 and 2, the relative reactivities of the $C_7H_7^+$ ion with DMA, ethylbenzene, and toluene were calculated to be 5.7, 2.1, and 1.0 respectively.

However, *N*,*N*-dimethyltropylamine, which is expected to be formed by the reaction of a tropylium ion with DMA, was not detected among the products under these experimental conditions except for the case of the cycloheptatriene–DMA mixture.[20)]

$C_7H_7^+$ Ion from Ethylbenzene. Although a tropylium ion was not captured in the gas-phase radiolysis of alkylbenzenes, the possibility still remains that a tropylium ion is formed as an intermediate and that it reacts with the substrate after being rearranged to a benzyl ion. Since the deuterium-labeling study would be expected to present instructive information in this respect, ethylbenzene-α-d_2 and toluene-α-d_3 were irradiated in the presence and in the absence of DMA, and the NMR and mass spectra of the DMBA, EDPM, and MDPM thus produced were measured. The results obtained from these measurements are shown in Table 2 and Fig. 3.

The mass spectra of the DMBA formed in the gas-phase radiolysis of an ethylbenzene-α-d_2–DMA mixture agreed very closely with that of authentic *N*,*N*-dimethylbenzylamine-α-d_2, suggesting that the precursor ion for this product is the $C_7H_5D_2^+$ ion formed by the loss of β-methyl from the original molecular ion without involving any isotopic mixing between β-methyl and benzyl groups (Fig. 3). Although the mass spectra of the EDPM formed in the gas-phase radiolysis of

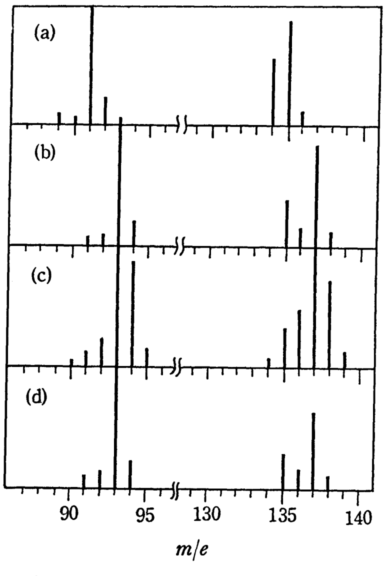
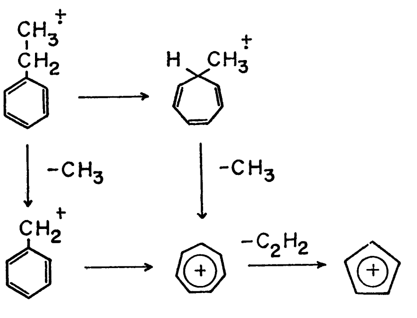


Fig. 3. Partial mass spectra of (a) authentic DMBA-d_0, (b) authentic DMBA-α-d_2, (c) DMBA formed in the gas-phase radiolysis of a toluene-α-d_3-dimethylamine mixture, and (d) DMBA formed in the gas-phase radiolysis of an ethylbenzene-α-d_2-dimethylamine mixture.

pure ethylbenzene-α-d_2 were not analyzed because of its complexity resulting from the scrambling of this compound in the mass spectrometer, it seems reasonable to conclude on the basis of Eqs. (1)—(3) that the precursor ion for this product is also the $C_7H_5D_2^+$ ion.

The NMR data provide an important clue to the information on the isotopic distribution in these products. The ratios of the methylene protium atoms to the total phenyl protium atoms in DMBA and EDPM were determined and converted into the ratio of the methylene protium atoms to phenyl protium atoms of the benzyl group originating from the $C_7H_5D_2^+$ ion. If the $C_7H_5D_2^+$ ion took a symmetrical structure, that of a tropylium ion or another possible ion, the protium and deuterium atoms of the benzyl group of both products would be statistically distributed between the methylene and phenyl units and the H_{CH_2}/H_{Ph} ratio would be 0.40. On the other hand, if the $C_7H_5D_2^+$ ion were the benzyl ion retaining the original structure, no protium atoms would be introduced to the methylene group of either product. Since the observed H_{CH_2}/H_{Ph} ratios are between these two values except for one case (ethylbenzene-α-d_2 2.2 mmHg, DMA 3.8 mmHg), it may be suggested that a partial hydrogen scrambling occurs in the $C_7H_5D_2^+$ ion. The degree of scrambling calculated is also shown in Table 2.

On the other hand, in the mass spectrometric studies of ethylbenzene it has been proposed that the $C_7H_7^+$ ion, which undergoes further decomposition, is a tropylium ion, though the timing when ring expansion occurs is obscure, as is shown in Scheme 1.[21)]



Scheme 1.

On the basis of the present observation, however, it seems reasonable to conclude that the $C_7H_7^+$ ion is formed as a benzyl ion by a loss of β-methyl from the ethylbenzene molecular ion before the ring expansion of the molecular ion. The benzyl ion thus formed reacts rapidly with DMA to produce DMBA without involving hydrogen scrambling when DMA is present at a higher pressure. When, in the absence of DMA, the $C_7H_7^+$ ion reacts with ethylbenzene, which has a lower reactivity to the ion, a hydrogen scrambling of the $C_7H_7^+$ ion may come to compete with the product formation. Such a hydrogen scrambling may occur *via* a tropylium ion, as has been suggested by the mass-spectrometric studies. For each experiment, the extent of scrambling was determined and plotted against the pressure of ethylbenzene, as is shown in Fig. 4. The extent of scrambling depends on the reaction system; the scrambling becomes more remarkable as the pressure of ethylbenzene decreases, while the scrambling is completely depressed in the presence of enough DMA (3.8 mm) in the reaction system.

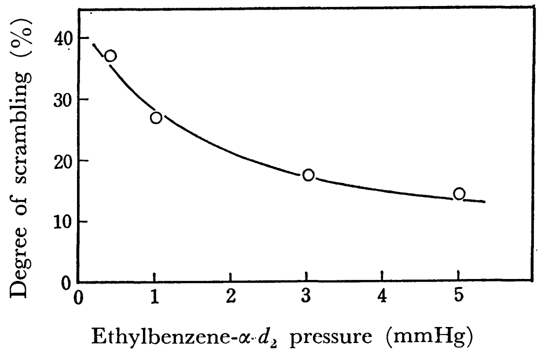
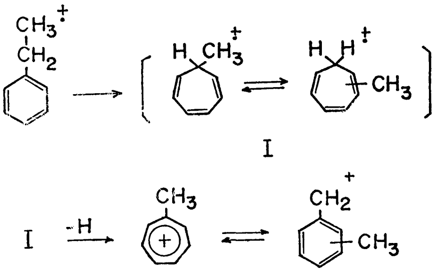


Fig. 4. Pressure effect on scrambling of EDPM formed in the gas-phase radiolysis of ethylbenzene-α-d_2.

It is likely that the mechanism described above is also supported by the formation of a product derived from the $C_8H_9^+$ ion from ethylbenzene. It has been suggested in the mass-spectrometric investigations[22)] that the $C_8H_9^+$ ion from ethylbenzene undergoes an extensive scrambling of the ring and α-hydrogen atoms, and that this scrambling is caused by a ring expansion from the ethylbenzene ion to the methylcycloheptatriene ion, followed by hydrogen shift, before the loss of the hydrogen (Scheme 2).

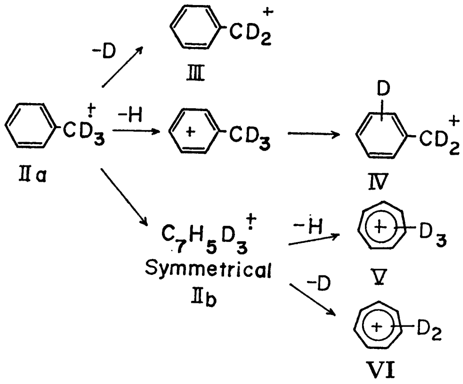


Scheme 2.

If the methyltropylium ion were formed in this manner in the gas-phase radiolysis of ethylbenzene, this ion would be expected to rearrange to the xylyl ion,[23)] which would react with DMA to produce *N*,*N*-dimethylxylylamines. However, no *N*,*N*-dimethylxylylamines were detected among the reaction products; *N*,*N*-dimethyl-α-phenetylamine was observed instead. The precursor ion for *N*,*N*-dimethyl-α-phenetylamine is presumably the α-phenetyl ion, which is formed either by a hydrogen loss from the ethylbenzene ion or by a hydride transfer from ethylbenzene to any primary ion, and which does not rearrange to the methyltropylium ion nor to xylyl ions. Therefore, it may be concluded that the rearrangement from the ethylbenzene ion to the methylcycloheptatriene ion does not occur, at least not under the present radiolytic conditions.

$C_7H_7^+$ Ion from Toluene. As is shown in Fig. 3, the mass spectra of the DMBA formed in the gas-phase radiolysis of a toluene-α-d_3–DMA mixture is different

from that of authentic *N*,*N*-dimethylbenzylamine-α-d_2, indicating that both DMBA-d_2 and DMBA-d_3 are formed. The ratio of DMBA-d_2 to DMBA-d_3 was calculated to be 1.2 from relative intensities of the ions in the molecular ion region and the region corresponding to the $C_7H_7^+$ ion. This ratio also indicates that of $C_7H_5D_2^+$ to $C_7H_4D_3^+$. From the NMR spectrum, the ratio of the methylene protium atoms to the phenyl protium atoms was determined to be 0.14. The observed value suggests that a partial isotope scrambling occurs in the precursor ions of DMBA. The results can be explained by assuming the following scheme:



Scheme 3.

The benzyl ions, III and IV, are formed by the direct dissociations of D and H respectively from the molecular ion, IIa; the second dissociation is followed by a rapid intramolecular D^- transfer from the methyl to the phenyl group. These ions rapidly react with DMA to produce DMBA before the isomerization to tropylium ions occurs, since the concentration of DMA is high enough (12 mmHg). On the other hand, the tropylium ions, V and VI, are formed by the loss of H and D respectively *via* the symmetrical intermediate, IIb, as has previously been proposed by Meyerson. These tropylium ions also produce the DMBA, in which the deuterium atoms are statistically distributed in the benzyl groups *via* the isomerization to the benzyl ions. The benzyl ions, III and IV, produce DMBA containing five and four H_{Ph} respectively and no H_{CH_2} in the benzyl group. When *i* represents the isotope effect (k_H/k_D) on the hydrogen loss from the symmetrical intermediate, IIb, the ratio of V to VI is $3/5i$; the numbers of H_{Ph} and H_{CH_2} in the benzyl group of the DMBA originating from these ions are given by $5[(5\times 3)+(4\times 5i)]/7(5i+3)$ and $2[(5\times 3)+(4\times 5i)]/7(5i+3)$ respectively. On the other hand, the experimental values for H_{Ph} and H_{CH_2} in the benzyl group of the DMBA formed in the gas-phase radiolysis of a toluene-α-d_3-DMA mixture were calculated to be 4.0 and 0.56 respectively on the basis of the NMR and mass spectra. On the assumption of the wide range of *i*, 1∼4, the relative contributions of III, IV, and V and VI to the DMBA formation were calculated to be 28∼33, 33∼31, and 39∼36% respectively by correcting for the isotopic impurity in toluene-α-d_3.

The results for the MDPM formed in the gas-phase radiolysis of toluene-α-d_3 in the absence of DMA were treated in a similar manner; the relative contributions of III, IV, and V and VI to the MDPM formation were thus calculated to be 30∼37, 39∼29, and 33∼31% respectively.

Aspects of the Mechanism. In the radiolysis of toluene, the degree of scrambling estimated from the DMBA formation agreed approximately with that from MDPM as described above; about one-third of the $C_7H_7^+$ ion leading to the product formation is a scrambled ion. This coincidence might be attributed to the fact that scrambling occurs only by a ring expansion from the toluene molecular ion to a symmetrical cycloheptatriene-like intermediate, not by isomerization from the benzyl ion to the tropylium ion. The reason for this is that, in the radiolysis of ethylbenzene-α-d_2, the benzyl ion formed by direct dissociation was trapped without involving as much isomerization in the presence of DMA as in the radiolysis of the toluene system. If the isomerization of the benzyl ion to a tropylium ion occurs, some differences in the degree of scrambling should be observed between the DMBA and MDPM formation, since this scrambling process competes with product formation, in which the reactivities of the $C_7H_7^+$ ion to DMA and toluene are different, as has been shown previously.

However, the scrambling is, generally, not so significant in the gas-phase radiolysis of toluene and ethylbenzene as in the mass spectrometry. As reasons why such a disagreement is observed, two factors may be considered; (i) the difference in the magnitude of the internal energy of the molecular ion, and (ii) the difference in such conditions as the pressure; these factors are both concerned with the lifetime of the ion. As for (i), in the fields of mass spectrometry Howe and McLafferty[7)] have repoted that the degree of scrambling decreases with an increase in the internal energy; thus, in the case of toluene the direct dissociation of α-hydrogen becomes significant compared with the scrambling process. Assuming that the molecular ion fromed in the gas-phase radiolysis posseses greater internal energy, the question seems to be answered in a satisfying manner. Furthermore, with regard to (ii), the benzyl ion formed by such a direct dissociation comes to isomerize to a tropylium ion when the pressure of the substrate is low (Fig. 4) or when the rate of the product formation is slow (trapping by aromatics). These possibilities may become large under the conditions in a mass spectrometer.

Finally, a distinction between toluene and ethylbenzene in the $C_7H_7^+$-ion-formation process may be considered; the ethylbenzene ion does not rearrange to a symmetrical molecular ion, while a part of the toluene ion does. This difference can be explained in terms of the lifetimes of molecular ions. Since the ethylbenzene ion, in which the β C–C bond fission occurs with greater facility,[24)] is probably more short-lived than the toluene ion, the scrambling path cannot compete with the direct dissociation. The benzyl ion thus formed is rapidly trapped by the successive ion-molecule reaction with ethylbenzene or DMA, without involving any significant unimolecular isomerization when enough of these trapping agents are present in the reaction system.

We wish to thank Dr. Seung Geon Kim for his advice on the preparation of toluene-α-d_3 and ethylbenzene-α-d_2. Thanks are also due to Mr. Yoshio Takai and Mr. Norio Kimura for their measurements of the NMR and mass spectra respectively, and Mr. Tomikazu Sawai and Mr. Tamotsu Yamamoto for the γ irradiations.

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20) The formation of *N,N*-dimethyltropylamine was also observed in the gas-phase radiolysis of 7-methylcycloheptatriene-DMA mixture. These results will be described in a separated paper.

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23) This rearrangement is analogous to that from tropylium ion to benzyl ion, and it was also observed in the radiolysis of xylene-DMA mixtures.

24) This correlation is compatible with the relative intensities of M^+ to $C_7H_7^+$ in the mass spectra of both compounds; the ratio in ethylbenzene (0.32) is smaller than that in toluene (0.74), indicating that the ethylbenzene ion decomposes more rapidly to $C_7H_7^+$ ion than toluene ion does.