# Rare-Gas-Sensitized Radiolysis of Toluene

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The Ar-, Kr-, and Xe-sensitized radiolyses of toluene was studied at room temperature in the gas phase. The discussion was concentrated on the formation of three isomers of methyldiphenylmethane (MDPM), which, it had been suggested in a previous paper on the direct radiolysis of toluene, were formed by the ion-molecule reaction of $C_7H_7^+$ ions. The sensitization effect on the MDPM formation was extremely large in the case of Ar, and decreased in the order of Ar, Kr, and Xe. These results were explained in terms of charge transfer from these rare gases to toluene, resulting in the formation of the $C_7H_7^+$ ions. The isomer distribution of MDPM's in the rare-gas-sensitized radiolysis was considered on the basis of the reaction mechanism proposed previously. The sensitization effect on the formation of other products was also discussed briefly.

In the gas-phase radiolysis, ionic species formed by irradiation play significant roles in the product formation; therefore, mass spectrometric studies have provided valuable information about the primary process of the gas-phase radiolysis. In the case of simple alkylbenzenes, such as toluene, ethylbenzene, and xylenes, the most abundant ion in the mass spectra is the $C_7H_7^+$ ion,[1,2] and its reactions in the gas-phase radiolysis of these alkylbenzenes have been expected to be important. It was suggested, in previous papers on the gas-phase radiolysis of toluene, ethylbenzene, and *m*-xylene, that the $C_7H_7^+$ ions react with parent alkylbenzene molecules to form the corresponding benzylated alkylbenzenes, which are the major products of these radiolyses.[3-5] Furthermore, the mechanism of such an electrophilic substitution reaction of aromatic nuclei caused by the $C_7H_7^+$ ions was discussed on the basis of the isomer distribution and the pressure dependence of the yields of the products, methyldiphenylmethanes (MDPM's), in the gas-phase radiolysis of toluene.[4] The present investigation of the rare-gas-sensitized radiolysis of toluene has been carried out in order to obtain additional information about the mechanism of the formation of MDPM's in the radiolysis of toluene. In the rare-gas-sensitized radiolysis, the product distribution is often characteristic of the kinds of rare gases, and the investigations of such experiments using various rare gases are of value in connection with the study of the primary process of the radiolysis.

## Experimental

The toluene was the same as that used in a previous study.[4] The rare gases were obtained from Takachiho Shoji Co. and were used without further purification. The stated purities were 99.999%, 99.9%, and 99.9% for Ar, Kr, and Xe respectively. The experimental procedures were almost identical with those reported previously.[4] The irradiation cells were Pyrex cylinders approximately 120 m*l* in volume, and irradiations were carried out at room temperature with a 5000 Ci cobalt-60 source. The dose rate at the dose for toluene were $3.1\times10^{15}$ eV/hr·$\mu$mol and $7.4\times10^{16}$ eV/$\mu$mol respectively. The irradiated samples were analyzed with a gas chromatograph using a flame-ionization detector after the gas fraction volatile at $-120$°C (rare gas and the product gases) had been removed; all the liquid products except dimers were analyzed with a 3-m Apiezon L column at 100°C, while for dimers a 6-m mixed nitrate column[6] was used with temperature programming from 60 to 120°C. The experimental details were presented in a previous paper.[4]

## Results

As has previously been reported,[4] the products detected in the gas-phase radiolysis of toluene were hydrogen, methane, ethane, acetylene, benzene, ethylbenzene, xylenes, bibenzyl, and MDPM's, though in this study the gaseous products were not analyzed. The effect of the added rare gases, Ar, Kr, and Xe, on the product yields was studied at an almost constant pressure of toluene, $10.1\pm0.3$ mmHg; the results are presented in Table 1. Approximately linear relationships exist between the product yields and the pressure of the added rare gas, although some scattering was observed. From these results, the sensitization $G$ values, $G_s$, indicating the increases in the $G$ values of the products on the basis of the energy absorbed by the rare gas, were calculated; they are presented in Table 2.[7] As is shown in this table, $G_s$ (MDPM's) is extremely large in the Ar-sensitized radiolysis, and also has a considerable value in the case of Kr. In both cases, the sensitization effect is largest on the formation of MDPM's. On the other hand, in the Xe-sensitized radiolysis, the $G_s$ (MDPM's) value is very small and most of the MDPM's may be formed by the direct absorption of energy by toluene.

The isomer distribution of the MDPM's was approximately independent of the pressure of rare gas within

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

2) Much attention has been paid to the structure and formation process of the $C_7H_7^+$ ions because of the isotope randomization observed in the mass spectra of labeled alkylbenzenes, and the $C_7H_7^+$ ions are believed to have a tropylium-ion structure (see Ref. 1).

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

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

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

6) W. W. Hanneman, C. F. Spencer, and J. F. Johnson, *Anal. Chem.*, **32**, 1386 (1960).

7) The dose rate for rare gases was determined by correcting for the electron densities of rare gases relative to toluene.

TABLE 1. THE EFFECT OF THE ADDED RARE GAS ON THE PRODUCT YIELDS IN THE GAS PHASE RADIOLYSIS OF TOLUENE

| Added Rare Gas | Pressure, mmHg | | G value | | | | |
|---|---|---|---|---|---|---|---|
| | Rare gas | Toluene | Benzene | Ethylbenzene | Xylenes[a] | Bibenzyl | MDPMs[a] |
| — | — | 10.2 | 0.17 | 0.05 | 0.06 | 0.03 | 0.43 |
| Ar | 29.3 | 10.2 | 0.43 | 0.10 | 0.14 | n.d.[b] | 3.0 |
| | 50.0 | 10.0 | 0.65 | 0.15 | 0.21 | n.d.[b] | 4.6 |
| | 79.4 | 9.9 | 0.83 | 0.17 | 0.25 | n.d.[b] | 6.2 |
| | 99.7 | 10.4 | 1.28 | 0.28 | 0.36 | n.d.[b] | 9.9 |
| Kr | 30.8 | 9.8 | 0.44 | 0.15 | 0.17 | 0.07 | 1.0 |
| | 52.8 | 10.3 | 0.62 | 0.22 | 0.25 | 0.09 | 1.1 |
| | 82.9 | 10.2 | 0.88 | 0.31 | 0.32 | 0.12 | 1.4 |
| | 100 | 9.8 | 0.91 | 0.34 | 0.30 | 0.13 | 1.5 |
| Xe | 31.9 | 10.4 | 0.63 | 0.31 | 0.23 | 0.17 | 0.55 |
| | 52.5 | 10.4 | 0.75 | 0.41 | 0.27 | 0.34 | 0.52 |
| | 82.4 | 10.2 | 1.3 | 0.76 | 0.39 | 0.50 | 0.58 |

a) Total yields of the three isomers. b) Not detectable.

TABLE 2. THE SENSITIZATION $G$ VALUES IN THE RARE GAS SENSITIZED RADIOLYSIS OF TOLUENE
(toluene pressure, 10.1±0.3 mmHg)

| Added rare gas | $G_s$[a] | | | | |
|---|---|---|---|---|---|
| | Benzene | Ethyl-benzene | Xylenes | Bibenzyl | MDPMs |
| Ar | 0.27 | 0.05 | 0.08 | 0 | 2.4 |
| Kr | 0.12 | 0.04 | 0.04 | 0.02 | 0.18 |
| Xe | 0.13 | 0.08 | 0.04 | 0.05 | 0.02 |

a) The increase of the product molecules per 100 eV energy absorbed by the added rare gas.

TABLE 3. THE ISOMER DISTRIBUTION OF MDPM

| Added rare gas | Rare gas pressure mmHg | Isomer distribution, % | | |
|---|---|---|---|---|
| | | 2-MDPM | 3-MDPM | 4-MDPM |
| — | — | 12 | 76 | 12 |
| Ar | 50.0 | 12 | 74 | 14 |
| Kr | 52.8 | 8 | 85 | 7 |
| Xe | 52.5 | 13 | 75 | 11 |

the limits of experimental error; the percentages of the three isomers at a rare-gas pressure of about 50 mmHg are presented in Table 3, together with those obtained in the direct radiolysis of toluene. In all cases, a large portion of the MDPM's consists of 3-MDPM; it is formed by benzylation at the *meta* position of toluene. The dependence of the $G_s$ values of the MDPM isomers on the toluene pressure was studied in the Ar- and Kr-sensitized radiolyses at constant rare gas pressures, 51.1 and 52.7 mmHg, of Ar and Kr respectively; the results are illustrated in Figs. 1 and 2. The pressure dependence of the $G$ values of the MDPM isomers in the previous study of the radiolysis of pure toluene obtained is also shown with dotted lines in Fig. 2 for the sake of comparison. In both the Ar- and Kr-sensitized radiolyses, $G_s$(3-MDPM) decreased with an increase in the toluene pressure, while $G_s$(2-MDPM)

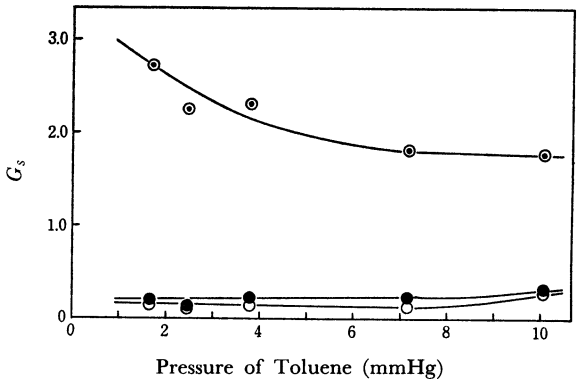



Fig. 1. The dependence of $G_s$(MDPM's) on toluene pressure in the Ar sensitized radiolysis at 51.1 mmHg of Ar pressure: ○, $G_s$(2-MDPM); ⊙, $G_s$(3-MDPM); ●, $G_s$(4-MDPM).

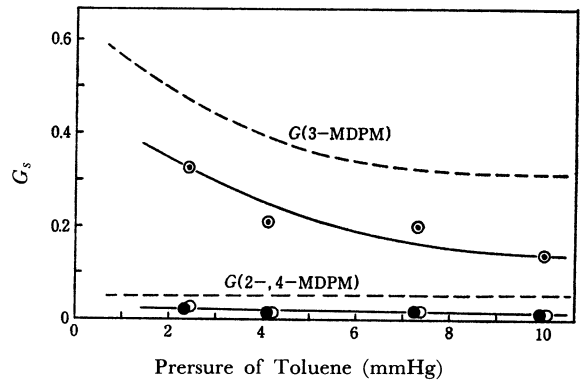



Fig. 2. The dependence of $G_s$(MDPM's) on toluene pressure in the Kr sensitized radiolysis at 52.7 mmHg of Kr pressure and that of $G$(MDPM's) in the radiolysis of pure toluene (dotted lines): ○, $G_s$(2-MDPM); ⊙, $G_s$(3-MDPM); ●, $G_s$(4-MDPM).

and $G_s$(4-MDPM) were not appreciably affected by the toluene pressure. Such pressure dependencies of the $G_s$ values of the MDPM isomers are similar to those of their $G$ values in the direct radiolysis.

## Discussion

The ionization potentials and the energy levels of the excited states of Ar, Kr, and Xe are shown in Table 4. Charge and excitation transfers from these states to toluene become the major modes of energy absorption by toluene molecules in the radiolysis of toluene in the presence of excess rare gas.

Table 4. Ionization potentials and excitation energies of rare gases (in eV)[a)]

| Rare gas | I.P. | | Allowed state | | Metastable state | |
|---|---|---|---|---|---|---|
| | $^2P_{3/2}$ | $^2P_{1/2}$ | $^3P_1$ | $^1P_1$ | $^3P_2$ | $^3P_0$ |
| Ar | 15.75 | 15.93 | 11.62 | 11.82 | 11.56 | 11.72 |
| Kr | 14.00 | 14.66 | 10.03 | 10.64 | 9.91 | 10.56 |
| Xe | 12.13 | 13.43 | 8.43 | 9.57 | 8.31 | 9.44 |

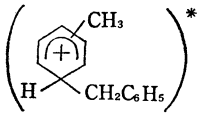
a) B. Brocklehurst, *Radiation Res. Rev.*, **1**, 225 (1968).

*The Sensitization on the Formation of MDPM's.* In the previous paper on the gas-phase radiolysis of toluene, the following mechanism of the formation of MDPM's has been proposed on the basis of the pressure dependence of the yields of the three isomers.[4,8)]

$$C_6H_5CH_3 \rightsquigarrow C_6H_5CH_3^{+*} + e \quad (1)$$

$$C_6H_5CH_3^{+*} \longrightarrow C_7H_7^+ + H \quad (2)$$

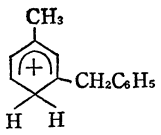
$$C_7H_7^+ + C_6H_5CH_3 \longrightarrow \left(\text{I}^*\right) \quad (3)$$




I*

$$I^* + C_6H_5CH_3 \longrightarrow \text{MDPM} + C_7H_9^+ \text{ (minor)} \quad (4)$$

$$\longrightarrow I + C_6H_5CH_3 \text{ (major)} \quad (5)$$




$$I \longrightarrow \text{Im} \quad (6)$$

Im

$$\text{Im} + C_6H_5CH_3 \longrightarrow \text{3-MDPM} + C_7H_9^+ \quad (7)$$

$$\longrightarrow \text{Adduct Ion} \quad (8)$$

where I* is an excited $\sigma$-complex producing three isomers of MDPM's, and where a less excited $\sigma$-complex, I, isomerizes to the most stable one, Im, which then produces 3-MDPM or a trimeric ion.

The $G_s$ values of the MDPM's exhibit remarkable differences among the Ar-, Kr-, and Xe-sensitized radiolyses; they decreased in the order of Ar, Kr, and Xe, as is shown in Table 2. Such results can be explained as follows. The appearance potential of the $C_7H_7^+$ ion from toluene is 11.8 eV,[1)] and the possible mode of its formation by the rare-gas sensitization is considered to involve a charge-transfer process (see Table 4):[9)]

$$X \rightsquigarrow X^+ + e \quad (9)$$

$$X^+ + C_6H_5CH_3 \longrightarrow X + C_6H_5CH_3^{+*} \quad (10)$$

$$C_6H_5CH_3^{+*} \longrightarrow C_7H_7^+ + H \quad (11)$$

where X shows a rare gas such as Ar, Kr, and Xe. The excess energies available in the charge transfers from the $^2P_{3/2}(^2P_{1/2})$ states of $Ar^+$, $Kr^+$, and $Xe^+$ to toluene (Reaction (10)) are 6.93 (7.11), 5.18 (5.84) and 3.31 (4.61) eV respectively (the ionization potential of toluene is 8.82 eV[10)]), and end up as excess internal energies in the resulting toluene ion. Therefore, the probability of the fragmentation of the excited toluene ions to the $C_7H_7^+$ ions (Reaction (11)), *i.e.*, the sensitization effect on the formation of MDPM's, depends on the ionization potentials of rare gases and increases in the order of Xe, Kr, and Ar.

If the added rare gas contributed to the collisional stabilization of the excited $\sigma$-complex, I*, one might expect a more selective formation of 3-MDPM in these rare-gas-sensitized radiolyses than in the direct radiolysis of toluene. However, the isomer distribution of MDPM's was not affected by the addition of rare gas, except in the case of Kr (to be discussed below) (Table 3) and was approximately independent of the rare gas pressure, as has been discussed above. On this basis, it seemed reasonable to conclude that the collisional stabilization of I* with rare gas atoms can hardly compete with the reactions of I* with toluene molecules, Reactions (4) and (5). Two explanations may be offered for this observation. First, and less likely, it may be suggested that the collisional stabilization of I* with rare gas is less effective than that with toluene because the toluene molecule possesses a higher degree of freedom. A second, and perhaps more likely, explanation would be that Reaction (5) is not a simple collisional stabilization, but a certain rapid chemical reaction, involving addition and dissociation or the benzyl-cation transfer from I* to another toluene molecule[11)] analogous to the proton transfer (Reaction (4)).

As is shown in Figs. 1 and 2, the dependence of the $G_s$ values of MDPM's on the toluene pressure in the Ar- and Kr-sensitized radiolyses is almost identical with the pressure dependence of the $G$ values of MDPM's in the radiolysis of pure toluene. Such a result also indicates that the isomer distribution of MDPM's was altered only by the change in the toluene pressure and was not appreciably affected by the addition of the rare gas. Thus, the results obtained in this study suggest that the effect of the added rare gas on the formation of MDPM's is small, if present at all, except for the sensitization upon the primary formation of the $C_7H_7^+$ ions.

When the isomer distributions of MDPM's in the Ar- and Kr-sensitized radiolyses are compared, the percentage of 3-MDPM is found to be somewhat larger in the latter case than in the former case (Table 3).

8) An analogous mechanism was also proposed in the study of the reactions of $C_3H_7^+$ ions with aromatic hydrocarbons [S. Takamuku, K. Iseda, and H. Sakurai, *J. Amer. Chem. Soc.*, **93**, 2420 (1971).].

9) The excitation transfer from the $^1P_1$ state of Ar may also contribute to the sensitization upon the formation of the $C_7H_7^+$ ions.

10) S. C. Lind, "Radiation Chemistry of Gases," Reinhold, New York (1961), p. 270.

11) In such a reaction, I* might act as a less electrophilic reagent to another toluene molecule to form a less energetic complex, I, as has previously been proposed (see Ref. 8).

Such a discrepancy in the Ar- and Kr-sensitized radiolyses might be attributed to the difference in the internal energy of the $C_7H_7^+$ ions formed through the charge transfer from these rare gases to toluene; the internal energy of the $C_7H_7^+$ ions formed through the charge transfers from Kr is smaller than that from Ar because of the lower exothermicity of Reaction (10), and the addition of the less excited $C_7H_7^+$ ion to toluene results in the formation of a less excited complex, producing 3-MDPM with a higher probability. In the Xe-sensitized radiolysis, most of the MDPM's may be formed by direct energy absorption by toluene; the isomer distribution was similar to that in the direct radiolysis, as is shown in Table 3.

*The Sensitization on the Formation of Other Products.* As has been previously reported, in the gas-phase radiolysis of toluene the primary processes leading to the formation of benzene, ethylbenzene, xylenes, and bibenzyl are considered to be as follows:[4]

$$C_6H_5CH_3 \rightsquigarrow C_6H_5\cdot + CH_3\cdot \quad (12)$$

$$C_6H_5^+ + CH_3\cdot + e \quad (13)$$

$$\cdot C_6H_4CH_3 + H \quad (14)$$

$$C_6H_5CH_2\cdot + H \quad (15)$$

Thus, both the phenyl radicals and the phenyl cations have been considered to give rise to benzene, and the formation of ethylbenzene, xylenes, and bibenzyl has been attributed to combinations of the radicals, involving methyl, tolyl, and benzyl radicals. With regard to these products, the $G_s$ values in the Ar-, Kr-, and Xe-sensitized radiolyses and the $G$ values in the direct radiolysis do not differ significantly (Tables 1 and 2). However, from the results shown in Table 2 it may be considered that the sensitization effect on the formation of benzyl radicals, producing ethylbenzene and bibenzyl, increases in the order of Ar, Kr, and Xe; in the Xe-sensitized radiolysis, bibenzyl, the minor dimeric product in the direct radiolysis, was formed in a yield comparable to that of MDPM's at a higher pressure of Xe Table 1. As has previously been reported, in the mercury-photosensitized decomposition of toluene vapor at 2537 Å, the $\beta$ C–H bond scission is a major primary process, as is the $\alpha$ C–C bond scission, and the only dimeric product detected is bibenzyl.[4] Thus, the distribution of the products formed by the Xe sensitization resembles that in the mercury-photosensitized decomposition rather than that in the direct radiolysis. Such a result may be attributed to the fact that the energy transferred from Xe to toluene in the sensitized radiolysis is smaller than those from Ar and Kr, and is also smaller than that directly absorbed by toluene.

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