BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2090—2095 (1971)

The Gas-Phase Radiolysis of Cycloheptatriene

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(Received February 12, 1971)

The γ radiolysis of cycloheptatriene (CHT) in the gas phase has been investigated as a function of the pressure (2—14 mmHg) and in the presence of various additives (NO, O_2, NH_3, N_2O, and C_3H_8). The G values obtained at 10.5 mmHg and at a total dose of 1.1×10^{19} eV are as follows: hydrogen, 0.50; methane, 0.16; acetylene, 1.52; cyclopentadiene, 0.29; benzene, 0.65; toluene, 1.68; dimers, 2.99. The yields of toluene and cyclopentadiene decrease with the pressure and are not appreciably affected by these additives; this suggests a contribution of the excited CHT molecules formed by direct excitation to their formation. The formation of dimers and benzene is affected by a radical scavenger (O_2, NO), indicating the importance of the radical processes. The reaction products obtained *via* a $C_7H_7^+$ ion, which is well known to be produced by the irradiation of CHT, have not been observed, while in the radiolysis of CHT in the presence of benzene and a radical scavenger, biphenylmethane has been produced, presumably by a reaction of the $C_7H_7^+$ ion with benzene. Therefore, it was assumed that the $C_7H_7^+$ ion produced from CHT does not contribute to the dimer formation, but may initiate the ionic polymerization.

Recently, much attention has been paid to ion-molecule reactions in the gas-phase radiolysis. Mass spectrometric studies provide useful information with regard to the ions produced in the gas-phase radiolysis. In the mass spectrometry of alkylbenzenes,[1] the most abundant ion has been observed to be a $C_7H_7^+$ ion ($m/e=91$), which has a completely symmetrical tropylium structure rather than that of benzyl, in common with these alkylbenzenes. In a previous paper,[2] it was observed that the $C_7H_7^+$ ion produced by the γ irradiation of toluene, ethylbenzene, and *m*-xylene vapors adds to the respective aromatic-ring, finally forming benzylated products, predominantly at a *meta* position to the resident alkyl group. Furthermore, the reaction mechanism has been discussed on the basis of electrophilic aromatic substitution in the gas-phase[3] and compared with the analogous isopropylation of benzene and toluene.[4]

In conjunction with these problems, we have recently investigated the γ radiolysis of cycloheptatriene (CHT) vapor, which is known, from mass spectrometric studies, to produce a $C_7H_7^+$ ion similar to those obtained from alkylbenzenes.[5] The present paper will describe the product formation and the reaction mechanism of this gas-phase radiolysis of CHT, though clear information about the structure and the reactivity of the $C_7H_7^+$ ion has not been obtained.

Experimental

Materials. CHT was prepared by the pyrolysis of 7,7-dichloronorcarane, which has been produced from cyclo-

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[1] H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. Mclafferty, Ed., Academic Press, New York, 1963, p. 453.

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

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

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

[5] S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957); S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 3340 (1963).

hexene;[6] it was distilled through a spinning-band column and then purified by preparative-scale gas chromatography using a 3-m PEG-6000 column at 65°C and, further, a 3-m DNP column at 65°C. Gas-chromatographic analysis on a 4.5-m PEG-6000 column showed the presence of toluene (0.024 mol%) and an unknown impurity (<0.07%). The purified CHT was degassed, dried over phosphorus pentoxide and a sodium mirror in a high-vacuum line, and then stored in a glass tube with a mercury cut-off at a low temperature.

Nitric oxide, nitrous oxide, and propane obtained from Takachiho Trading Co., and ammonia generated from 28% ammonia water were dried over a sodium mirror in a high-vacuum line and then purified by low-temperature distillations. The oxygen (minimum purity: 99.9%) was used without further purification.

Sample Preparation. The irradiation cells were Pyrex cylinders with a break-seal, approximately 105 m*l* in volume. Prior to the sample introduction, the cells were baked and evacuated overnight at a pressure of 10^{-6} mmHg. The pressure of the sample was measured by means of a mercury manometer; the pressure range was 2—14 mmHg. In the experiment with an additive, the amount of the additive was measured by a gas buret and transferred into the cell through a break-seal.

Irradiation and Dosimetry. Irradiation was carried out at room temperature with a 5000 Ci ^{60}Co source. Dosimetry was based on $G(C_2H_4 \rightarrow H_2) = 1.28$,[7] assuming that the energy distribution was proportional to the electron density. The dose rate in the present experiments was 3.82×10^{15} eV/hr·μmol (CHT). The G values in the runs with an additive were calculated on the basis of the energy absorbed by CHT alone. The total dose range was $(1.1—2.7) \times 10^{19}$ eV.

Analysis. The hydrogen yield in the product gas volatile at −196°C was determined from the volume difference measured with a standard Toepler pump and gas buret arrangement, before and after passage through a palladium thimble heated at ca. 300°C. The C_2—C_4 hydrocarbons volatile at −120°C were transferred into a capillary with a Toepler pump and analyzed gas-chromatographically using a 3-m silica gel column at 100°C. All the non-volatile products at −120°C except for dimers were identified by gas-chromatographic comparison with authentic samples using several columns (PEG-6000, DNP, and APL). The dimers were identified by means of a gas chromatograph-mass spectrometer combination, but the structures were not investigated except that of bitropyl. The yields of the gaseous and liquid products were determined by a comparison of the peak areas with those for known amounts of propane and benzene respectively, which were submitted to gas chromatography before each analysis.

Results

The product yields in the irradiated CHT at 10.5 mmHg are shown in Table 1, together with those of the radiolysis of toluene vapor.[3] The observed gaseous products were hydrogen, methane, and acetylene. The yields of ethylene and ethane were negligibly small. Cyclopentadiene, benzene, toluene, and several kinds of dimers were also formed as liquid products, though a part of the cyclopentadiene was observed in the dimeric form because of the instability of the monomer at room temperature. Several dimers whose carbon

Table 1. Yields in the γ radiolysis of cycloheptatriene vapor at room temperature and comparison with those of toluene vapor

	Cycloheptatriene[a)]		Toluene[b)]
	Pressure, mmHg		
	10.5	10.5	10.7
	Dose, 10^{19} eV		
	1.1	2.7	1.9
Products	G value		
H_2	0.50	c)	0.36
CH_4	0.16	c)	0.15
C_2H_2	1.52	1.49	0.41
C_2H_4	trace	trace	trace
C_2H_6	trace	trace	0.07
Cyclopentadiene	0.29	0.19	d)
Benzene	0.65	0.52	0.18
Toluene	1.68	1.50	—
Dimers	2.99	c)	0.47

a) This work, b) Ref. 4, c) Not determined, d) Not detected.

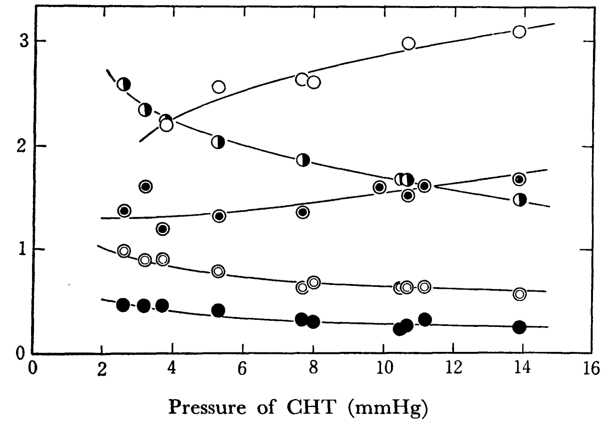

Fig. 1. The pressure dependence of the products yields in the radiolysis of cycloheptatriene vapor: ⊙, C_2H_2; ●, Cyclopentadiene; ◎, Benzene; ◑, Toluene; ○, Dimers.

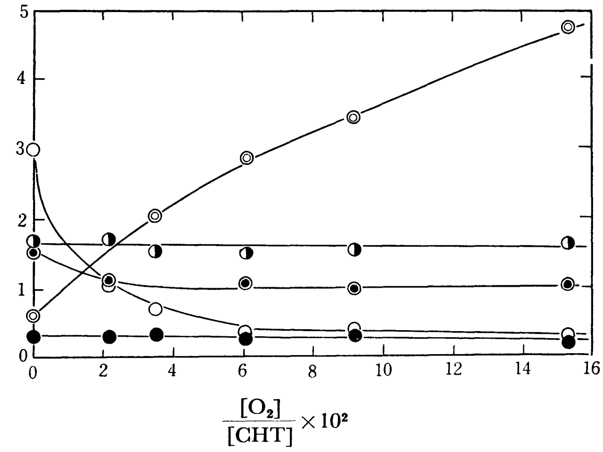

Fig. 2. The effect of an added O_2 in the radiolysis of cycloheptatriene vapor at 10.5 mm: ⊙, C_2H_2; ●, Cyclopentadiene; ⊙, Benzene; ◑, Toluene; ○, Dimers.

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[6] G. C. Robinson, *J. Org. Chem.*, **29**, 3433 (1964); H. E. Winberg, *ibid.*, **24**, 264 (1959).

[7] R. A. Back, T. W. Woodward, and K. A. Mclauchan, *Can. J. Chem.*, **40**, 1380 (1962).

TABLE 2. THE EFFECTS OF ADDITIVES IN THE γ RADIOLYSIS OF CYCLOHEPTATRIENE VAPOR AT 10.5 mmHg

	None	NO		N_2O		NH_3		C_3H_8	
		Mol %							
		2.9	4.7	3.5	10.5	5.4	8.5	8.3	12.8
	G value[a)]								
H_2	0.50	0.58	0.58	0.55	0.41	0.50	0.56	b)	b)
CH_4	0.16	b)	b)	b)	b)	0.12	0.05	b)	b)
C_2H_2	1.52	1.07	1.07	1.30	1.21	1.10	0.89	b)	b)
Cyclopentadiene	0.29	0.36	0.33	0.25	0.28	b)	0.31	0.24	0.24
Benzene	0.65	1.55	1.94	0.58	0.68	b)	0.57	0.65	0.65
Toluene	1.68	1.73	1.66	1.57	1.62	b)	1.64	1.58	1.68
Dimers	2.99	1.63	0.96	2.85	b)	3.25	2.85	b)	b)

a) The G values are calculated on the basis of energy absorbed by CHT alone. The total dose is 1.1×10^{19} eV.
b) Not determined.

number might be fourteen were detected gas-chromatographically, though the structure have not determined except for that of bitropyl.[8)] The G value of the total dimers is calculated on the assumption that the sensitivity of the detection of dimers is equal to that of bitropyl.

The effect of the total dose was small except in the case of cyclopentadiene at a CHT pressure of 10.5 mmHg over the dose range from 1.1×10^{19} to 2.7×10^{19} eV, as is shown in Table 1. The product yields at a dose of 1.87×10^{17} eV/μmol (CHT) as a function of the CHT pressure are shown in Fig. 1. Though the results for hydrogen and methane are not shown in the figure, $G(H_2)$ and $G(CH_4)$ were essentially unaffected by the CHT pressure.

The experimental results obtained in the presence of an additive, *i.e.*, oxygen, nitric oxide, nitrous oxide, ammonia, or propane, are shown in Fig. 2 and Table 2. Of particular interest is the remarkable increase in the G value of benzene upon the addition of nitric oxide and oxygen. When iodine was added to CHT, the formation of benzene was also observed without γ irradiation, while in the case of oxygen no such behavior was observed. Another significant feature in the additive experiment is the notable decrease in the yield of the dimer upon the addition of a radical scavenger (NO or O_2).

The γ radiolysis of binary mixtures of CHT and benzene was carried out in the presence of nitric oxide (10 mol%). Biphenylmethane and biphenyl were produced with G values of 0.069 and 0.094 respectively, as determined on the basis of the energy absorbed by CHT at a [CHT]/[benzene] molar ratio of 0.466.

Discussion

In the gas-phase radiolysis of CHT, the observed products were hydrogen, methane, acetylene, cyclopentadiene, benzene, toluene, and dimers; Table 1 lists those products together with the results on toluene.[3)] The yields of the radiolytic products from CHT were, in general, large compared with those from toluene, especially those of acetylene, benzene, and dimers. Furthermore, cyclopentadiene was a new product which was not observed in the radiolysis of toluene. In the mass-spectrometric studies[1)] of these isomeric compounds (CHT and toluene), it is well known that the $C_7H_7^+$ ions are the most abundant in these compounds. However, the present observations seem to show that the common intermediate does not always produce the same final products in both the reaction systems, as will be discussed later. In the liquid-phase radiolysis of CHT, relatively low G values of gaseous products have been reported by Arai *et al.*,[9)] and the main reaction was a polymer formation, though the yields of the liquid products were not measured.

Formation of Toluene. As for the radiolytic products from CHT vapor, a fairly large amount of isomerization to toluene was observed, as has been reported in the photolysis[9,10)] and pyrolysis[11)] of CHT. The toluene formation is essentially unaffected by the addition of appreciable amounts of various scavengers, *i.e.*, oxygen and nitric oxide for radicals, nitrous oxide for electron, ammonia for positive-ions, and propane as a hydride-transfer agent to a positive ion, as is shown in Fig. 2 and Table 2. Thus, it is most reasonable to assume that radicals and positive-ions may be excluded as precursors of toluene in the radiolysis of CHT vapor. On the other hand, an electronically- or vibrationally-excited CHT molecule has been shown to easily isomerize to toluene in photolytic investigations in the gas phase.[9,10)] From these results, a direct excitation process such as this seems most reasonable:

$$\text{CHT} \rightsquigarrow \text{CHT}^* \qquad (1)$$

$$\text{CHT}^* \longrightarrow \text{Toluene} \qquad (2)$$

$$\text{CHT}^* + \text{CHT} \longrightarrow 2\,\text{CHT} \qquad (3)$$

The isomerization to toluene (reaction (2)) is presumed to compete with the collisional deactivation (reaction (3)). The steady-state treatment of reactions (1), (2) and (3) gives Eq. (I):

$$1/G(\text{Toluene}) = 1/G^\circ(\text{Toluene})\{1+k_3/k_2[\text{CHT}]\} \qquad (\text{I})$$

where G^0 (Toluene) is the G value of toluene at zero

[8)] Bitropyl was prepared by the method of Doering and Knox. (mp 61.8°C) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **79**, 352 (1957).

[9)] S. Arai, M. Maemori, K. Yamaguchi, and S. Shida, This Bulletin, **36**, 590 (1963).

[10)] R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 3432 (1962).

[11)] W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

pressure. According to Eq. (I), a plot of $1/G$(Toluene) *vs.* the CHT pressure should give a straight line with a slope of $1/G^0 \cdot k_3/k_2$. Such a plot is shown in Fig. 3, from which the ratio of the rate constant of the deactivation and that of the isomerization, k_3/k_2, as determined by the method of least squares, is found to be 0.051 mmHg^{-1}.

In the mercury-sensitized photolysis of CHT vapor by Arai *et al.*,⁹⁾ and in the direct photolysis by Srinivasan,¹⁰⁾ a similar kinetic treatment has been carried out. An interesting point is that the value of k_3/k_2 is greater in the photolysis than in the radiolysis; furthermore, it is greater at 3130 Å than at 2600 Å, or in the mercury-sensitized photolysis at 2537 Å, in which the value was 0.11 mmHg^{-1}. This means that the higher the energy provided to the CHT molecule, the shorter the lifetime of the active intermediate leading to the toluene formation and quenched poorly by collision, though the nature of the excited state is not clear in the present study. The G value of toluene extraporated to zero pressure is 2.6 in Fig. 3, indicating the G value of the excited CHT which isomerizes to toluene if it is not quenched by collisions.

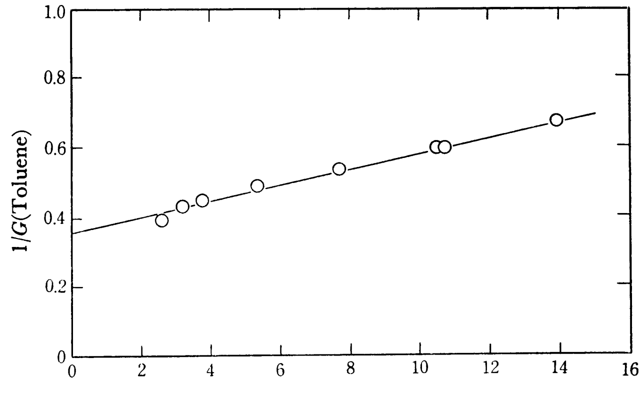


Fig. 3. Kinetic plots of $1/G$(Toluene) *vs.* pressure in the radiolysis of cycloheptatriene vapor.

Formation of Dimers. In the radiation chemistry of liquid hydrocarbon, a dimer which contains two hydrogen atoms less than the starting material has been observed as one of the typical products. For example, the bitropyl obtained from the radiolysis of liquid CHT has been observed to be formed *via* a symmetrical intermediate, the tropyl radical,[11] which has also been reported in the ESR study of the electron irradiated CHT at −196°C.[9] In the present study, bitropyl was not a predominant dimer, but many other dimers were produced to a similar extent, though their structures were not identified. The total dimer yields rapidly decreased upon the addition of oxygen and nitric oxide (Fig. 2 and Table 2), but the isomer distribution remained the same. It is generally assumed that the major effect of oxygen and nitric oxide on the product formation is due to the scavenging of free radicals, though it has been observed in some cases that nitric oxide acts as a charge-transfer agent,[12] since nitric oxide has an ionization potential (9.2 eV)[13] lower than those of many hydrocarbons. However, the decrease upon the addition of oxygen, which has a high ionization potential (12.1 eV),[13] strongly suggests a radical mechanism for the formation of dimers. On the other hand, CHT is also an efficient radical scavenger, so primarily-produced hydrogen atoms and hydrocarbon radicals may be almost all scavenged by CHT even in the absence of a radical scavenger:

$$\mathrm{CHT} \rightsquigarrow \mathrm{C_7H_7\cdot} + \mathrm{H} \qquad (4)$$

$$\mathrm{H} + \mathrm{CHT} \longrightarrow \mathrm{C_7H_9\cdot} \qquad (5)$$

$$\mathrm{C_7H_7\cdot} + \mathrm{CHT} \longrightarrow \mathrm{C_{14}H_{15}\cdot} \qquad (6)$$

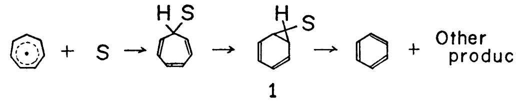
$$\mathrm{C_7H_9\cdot} + \mathrm{CHT} \longrightarrow \mathrm{C_{14}H_{17}\cdot} \qquad (7)$$

$$\mathrm{R\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{R{-}R} \qquad (8)$$

$$\longrightarrow \mathrm{RH} + \mathrm{R(-H)} \qquad (9)$$

where R is a monomeric or dimeric radical. It may be explained that many kinds of dimers are formed *via* these processes. These observations are obviously different from those for the dimer formation in the gas-phase radiolysis of toluene, in which the effect of nitric oxide is very small and in which ionic processes were predominant.[2,3]

Formation of Benzene. Benzene is a new product which was not reported in the photolysis of CHT vapor.[9,10] The G value of benzene decreased with an increase in the CHT pressure, though the pressure dependence is different from that of toluene. No significant effect on the yield was observed upon the addition of ammonia, propane, or nitrous oxide. Furthermore, it is an interesting fact that the addition of nitric oxide or oxygen remarkably increases the yield of benzene. These additional benzene yields are too large to be explained as the result of sensitization by nitric oxide or oxygen. It is assumed that the active species produced by the irradiation of CHT come to form benzene by means of the added nitric oxide or oxygen. Moreover, ionic species must be excluded, since the ultimate G value of the additional benzene which is obtained by the extrapolation of $1/\Delta G(\mathrm{C_6H_6})$ to the infinite concentration of oxygen as shown below is very large ($G_\infty(\mathrm{C_6H_6})=8.0$) compared to the G_e of CHT. Since nitric oxide and oxygen are both well known to act as radical scavengers, it seems to be most reasonable to expect the following radical process for the formation of the additional benzene:



(10)

where S is a radical scavenger. The norcaradiene-type intermediate (1) was previously suggested in the formation of benzene.[14,15] When a radical scavenger

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[12] R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **43**, 3814 (1965).

[13] K. Watanabe, *ibid.*, **26**, 542 (1957).

[14] M. E. Volpin, D. N. Kurzanov, and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960).

[15] T. Mukai, T. Nakazawa, and K. Okayama, *Tetrahedron Lett.*, 1695 (1968).

is absent in the system, tropyl radicals such as those produced by reaction (4) may undergo an addition reaction with CHT, as is shown in reaction (6), thus leading to the dimer formation. The fact that a radical scavenger competes with CHT for tropyl radicals is shown when we plot the yields of benzene and dimers against the concentration of a radical scavenger (Fig. 2). The yields of benzene were increased by an increase in the concentration, while the yields of the dimers were decreased. However, the correlation between these changes in the yields was not satisfactory. This cannot be explained well, but it may be partly caused by the different efficiencies in the dimer formation and the benzene formation from tropyl radicals. Since the reaction of tropyl radicals with CHT (reaction (6)) produces not only dimers but also high-molecular products, the efficiency of the dimer formation becomes relatively low.

A quantitative treatment of the formation of benzene in the presence of a radical scavenger is given by Eq. (II):

$$\frac{1}{\Delta G(\mathrm{C_6H_6})} = \frac{1}{G_1}\left(1 + \frac{k_6}{k_{10}}\cdot\frac{[\mathrm{CHT}]}{[\mathrm{S}]}\right) \qquad \text{(II)}$$

where $\Delta G(\mathrm{C_6H_6})$ is the difference in the G value of benzene, with and without a scavenger, and where G_1 is the G value of the C_7H_7 radical produced by reaction (4). In Fig. 4, $1/\Delta G(\mathrm{C_6H_6})$ is plotted against [CHT]/[S]. From the extrapolation of the straight line to the intercept, the ultimate yield of a tropyl radical (G_1) is observed to be 8.0. The mechanism of the formation of benzene from pure CHT is not clear, but such a free radical process seems to play a part. In this case, instead of oxygen or nitric oxide other small fragment radicals may act as radicals scavengers.

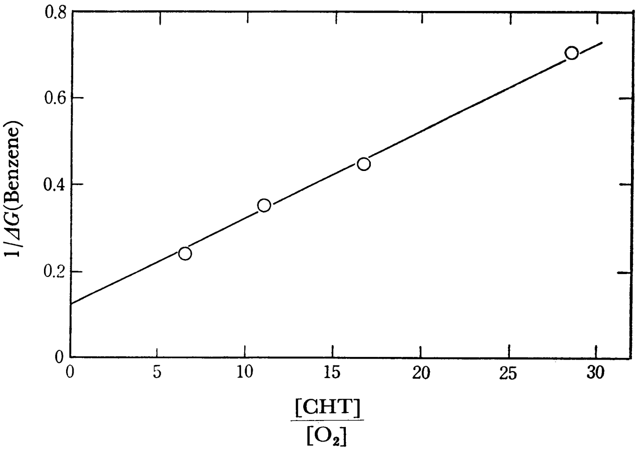


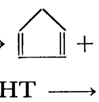
Fig. 4. Kinetic plots of $1/\Delta G$(Benzene) *vs.* [CHT]/[O_2] in the radiolysis of cycloheptatriene-O_2 mixtures.

Formation of Cyclopentadiene and Acetylene. In the mass spectrometry, a $C_5H_5^+$ ion, which could be a precursor of cyclopentadiene by a following hydride-transfer reaction, was reported to be produced by the secondary decomposition of a $C_7H_7^+$ ion:[1)]

$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2 \qquad (11)$$

However, under the radiolytic conditions, where the pressure is much higher compared than that of the mass-spectrometric conditions, a $C_7H_7^+$ ion is known to undergo a very fast ion-molecule reaction before its degradation to a $C_5H_5^+$ ion.[3)] Moreover, the formation of cyclopentadiene is essentially unaffected by the addition of various scavengers (NO, O_2, N_2O, NH_3, or C_3H_8), much as in the case of toluene. These observations suggest a direct excitation process of the formation of cyclopentadiene and acetylene:

$$\mathrm{CHT} \rightsquigarrow \mathrm{CHT^{**}} \qquad (12)$$

CHT** ⟶  + C_2H_2 (13)

$$\mathrm{CHT^{**}} + \mathrm{CHT} \longrightarrow 2\,\mathrm{CHT} \qquad (14)$$

The effect of the CHT pressure on the yield of cyclopentadiene (Fig. 1) was consistent with the above mechanism. The nature of the excited CHT molecule that decomposes to cyclopentadiene and acetylene may be energetically higher than that of a precursor of toluene, since they are poorly quenched by collision and since the process (reaction (13)) was not observed in either the photolysis or the pyrolysis.

On the other hand, acetylene is not only formed by reaction (13) but also by some other processes, because the $G(C_2H_2)$ value is much larger than that of cyclopentadiene and the pressure dependence is different from that of cyclopentadiene. The effects of additives were also observed (Table 2), but the other processes have not yet been clarified.

The Fate of the Tropylium Ion. It was one of the principal purposes of this work to determine the fate of the $C_7H_7^+$ ion generated in the γ radiolysis of CHT vapor. Unfortunately, in the radiolysis of pure CHT vapor information about this has not been obtained from direct evidence, such as the identification of the reaction products *via* the $C_7H_7^+$ ion.

In the mass-spectrometric studies of simple alkylbenzenes,[1,5)] it has been shown that the loss of an acetylene molecule (reaction (11)) is the only major decomposition process of the $C_7H_7^+$ ion at a low pressure. In the high-pressure mass spectrometry of toluene,[16,17)] it has been reported that the $C_7H_7^+$ and $C_5H_5^+$ ions decay exponentially with the pressure, thus giving a new product ion, $C_{14}H_{15}^+$, However, the $C_{12}H_{13}^+$ product ion, which would be formed by a similar addition reaction of the $C_5H_5^+$ ion to toluene molecules, is absent among the ions in the spectra observed at high concentrations of toluene. It seems reasonable to assume that the addition reaction of the $C_7H_7^+$ ion to toluene and the reaction (11) are competitive and that, in the radiolysis in which the pressure is relatively high compared to that in the ionization chamber of the mass spectrometer, the $C_7H_7^+$ ion exclusively adds to toluene. Consistent with these observation, it has been shown that methyldiphenylmethanes, which are the main dimeric products in the gas-phase radiolysis of toluene, are formed by such an addition of the $C_7H_7^+$ ion to toluene, while the addition

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16) S. Wexler and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 3940 (1968).

17) A. Giardini-Guidoni and F. Zocchi, *Trans. Faraday Soc.*, **64**, 2342 (1968).

products of the $C_5H_5^+$ ion are not present.[2,3] Moreover, it has been confirmed that the $C_7H_7^+$ ion adds also to benzene, which is added in the γ radiolysis of toluene, and thus produces diphenylmethane.[18] These observations suggest that aromatic compounds, such as benzene and toluene, are excellent reagents for the carbonium ion in the gas phase and that they produce relatively stable ions which finally change to the corresponding substituted alkylbenzenes. This technique might be useful for the investigation of the formation and the reactivity of the $C_7H_7^+$ ion in the radiolysis of CHT vapor. The preliminary results showed the formation of the expected biphenylmethane in the radiolysis of CHT vapor in the presence of benzene and a radical scavenger, though the G value was small (0.069). The low yield of diphenylmethane was supposed to be caused by the competitive reactions of the $C_7H_7^+$ ion with benzene and with CHT.

In the present investigation, though the precise reaction mechanism of the $C_7H_7^+$ ion is not yet clear, it is most reasonable to assume an ionic polymerization of CHT initiated by the $C_7H_7^+$ ion, for the dimeric products disappear upon the addition of a radical scavenger and CHT is expected to be subject to ionic polymerization, much as in the case of cyclopentadiene.[19] The mechanistic details of the reaction of the $C_7H_7^+$ ion are currently under investigation in these binary mixtures, CHT-benzene, CHT-toluene, and CHT-h_8-toluene-d_8.

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

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[18] K. Nakamura, S. Takamuku, and H. Sakurai, to be published.

[19] M. A. Bonin, W. R. Busler, and F. Williams, *J. Amer. Chem. Soc.*, **87**, 199 (1965).