The Radiolysis and Photolysis of Cycloheptatriene

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Previously we reported[1] that cyclooctatetraene is one of the most radiation-stable organic liquids. Henglein's experiment[2], in which the *G* value of the radical formation was determined by the addition of sulfur dioxide as the radical scavenger, also supports this conclusion. Although cyclooctatetraene resembles benzene in chemical structure, its chemical properties rather belong to the cycloolefins. Therefore, it would be interesting to investigate the radiolysis of cycloheptatriene C_7H_8, which is a cycloolefin with three alternant double bonds and one methylene group. There has been, to the author's knowledge, only one paper dealing with the radiolysis of cycloheptatriene. Juppe and Wolf[3] carried out the irradiation of carbon-14 labeled cycloheptatriene and found that randomly-labeled bitropyl is produced from specifically-labeled cycloheptatriene. They therefore suggested that a symmetrical intermediate is formed as a precursor of the dimer.

It is known that in many cases reactions in the radiation chemistry are similar to those involved in the photochemistry. The photochemical study of cycloheptatriene in the vapor phase is of considerable value for understanding the mechanism in the radiolysis. Recently Srinivasan[4] has found that toluene is mainly formed in its direct photolysis.

A more detailed study of the radiolysis and electron resonace study are presented here. Moreover, the mercury-photosensitized reaction of cycloheptatriene has been investigated in the expectation of elucidating the mechanism of the radiolysis.

Experimental

Material.—Cycloheptatriene was prepared by the thermal isomerization of bicycloheptadiene in the method described by Woods[5]. Repeated distillations were carried out to remove the by-products, especially toluene, from the raw material. However, the sample used here was shown to be 95 to 97% cycloheptatriene and 3 to 5% toluene by gas chromatography.

Irradiation.—The radiation employed in the radiolysis of liquid cycloheptatriene utilized γ rays from 200C ^{60}Co. The sample was degassed on a vacuum line by freezing and pumping, and then sealed off in a glass cell. Irradiations were made at room temperature for 3 to 14 days. The dose rate was about 3.9×10^3 r/min.

Analysis.—After irradiation the non-condensables at $-196°C$ (a mixture of hydrogen and methane) were transferred to a gas-buret by the use of a Toepler pump. Then the hydrogen and methane were analyzed by using a copper oxide furnace. The condensables were divided at $-120°C$ into two fractions, (a) $C_2\sim C_4$ hydrocarbons, and (b) C_7 hydrocarbons. Quantitative analysis of each fraction was accomplished by gas chromatography. The columns, consisting of benzyl ether and silicon oil on crushed firebrick support, enabled the complete separation of the compounds for fractions a and b respectively. After distillation of the volatile products in vacuo at 100°C, a viscous yellow residue was found on the wall of the glass cell. This substance was determined gravimetrically as the polymer.

ESR Experiments.—In the ESR experiments the radiation used was the electron beam from a 1.5MeV. Van de Graaff generator. The sample in an open vessel, which was kept at the temperature of liquid nitrogen, was irradiated with a dose of 1×10^8 rad. The spectra were observed also at $-196°C$ using a Nihon Denshikogaku ESR spectrometer.

Photochemical Experiments.—Cycloheptatriene vapor in a cylindrical quartz cell (diameter, 50 mm., length, 50 mm.), which contained a drop of

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[1] S. Shida, Y. Yamazaki and S. Arai, *J. Chem. Phys.*, 29, 245 (1958).

[2] A. Henglein, A/Conf., Vol. 29, 206 (1958).

[3] G. Juppe and A. P. Wolf, *J. Am. Chem. Soc.*, **83**, 337 (1961).

[4] R. Srinivasan, ibid., **84**, 3432 (1962).

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

mercury, was irradiated by a neon-gas-filled mercury lamp. The light shorter than 2200A was cut off with a filter. The analytical procedures were the same as in the radiolysis.

Results and Discussion

Mercury Photosensitized Reaction in the Vapor Phase.—Owing to the presence of impurities it was not possible to obtain the absorption intensity of cycloheptatriene at the wavelength of 2537A. However, the large absorption coefficient of mercury vapor for the radiation of 2537A led the authors to assume that it is predominantly the mercury photosensitized reaction which takes place.

Figure 1 shows the changes in total pressure as a function of the reaction time. Curves A and B are obtained for the initial pressures of 13.5 mmHg and 6 mmHg respectively. In run A a decrease in pressure of 2.2 mmHg was observed after the irradiation time of 300 sec., at which time the gas compositions were 30% toluene and 70% cyclcheptatriene. In run B a decrease of 2.0 mmHg was observed after 300 sec. The gas compositions were 75% toluene and 25% cycloheptatriene. In both cases the decomposition products were scarcely detectable. These results indicate that the major reaction is the isomerization of cycloheptatriene into toluene. The small decrease in total pressure may be attributed to the polymerization initiated by some radical decomposition of the cycloheptatriene.

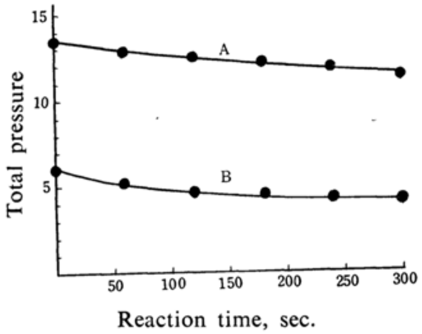

Fig. 1. Variation of total pressure as reaction time proceeds.
A Initial pressure, 13.5 mmHg
B Initial pressure, 6 mmHg

Figure 2 shows the amounts of toluene formed as the irradiation time proceeds. The initial pressure of cycloheptatriene is 7 mmHg. The amount of toluene increases as a linear function of the irradiation time.

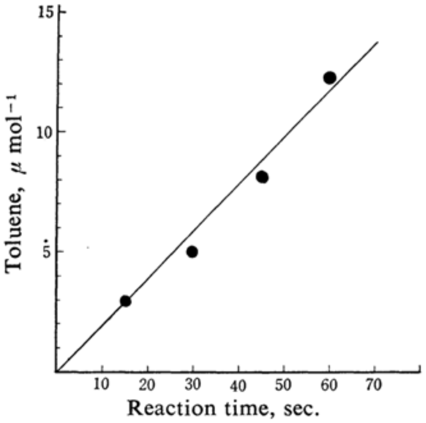

Fig. 2. Amounts of toluene formation as reaction time proceeds. The initial pressure of cycloheptatriene, 7 mmHg.

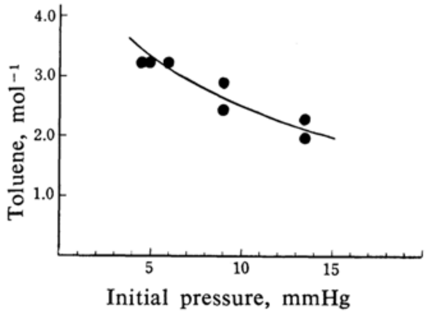

Fig. 3. Variation of toluene formation as a function of the initial pressure of cycloheptatriene. Irradiation time, 30 sec.

In Fig. 3 the amounts of toluene for the irradiation time of a half minute are plotted for the various initial pressures of cycloheptatriene. It may be clearly seen that the rates of toluene formation are strongly pressure-dependent. Thus, the present authors have concluded that, in the same manner as in cyclooctatetraene[6,7], an excited molecule of cycloheptatriene, which may either isomerize into toluene or be collisionally deactivated, is formed at the initial step. The experimental results may be explained by the following reaction mechanism:

$$C_7H_8 + Hg^* \rightarrow C_7H_8^* + Hg \qquad (1)$$

$$C_7H_8^* \rightarrow CH_3C_6H_5 \qquad (2)$$

$$C_7H_8^* + C_7H_8 \rightarrow 2C_7H_8 \qquad (3)$$

$$C_7H_8 + Hg^* \rightarrow \text{Polymerization initiated by radicals} \qquad (4)$$

The steady-state treatment leads to Eq. A:

$$\frac{I_o}{R_t} = 1 + \frac{k_3}{k_2}[C_7H_8] \qquad (A)$$

where R_t is the rate of toluene formation, I_o

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[6] H. Yamazaki and S. Shida, *J. Chem. Phys.*, **24**, 1278 (1956).

[7] H. Yamazaki, This Bulletin, **31**, 677 (1958).

is the absorbed intensity of the 2537A resonance line, $[C_7H_8]$ is the pressure of cycloheptatriene, and k_2 and k_3 are the rate constants of reactions 2 and 3 respectively. Thus, there has to be a linear relationship between $1/R_t$ and $[C_7H_8]$. As may be seen in Fig. 4, a satisfactory straight line is given. A slope-to-intercept ratio corresponds to k_3/k_2 in Eq. A. The numerical value is 0.11 mmHg^{-1}.

Srinivasan[4] has recently studied the direct photolysis of cycloheptatriene in the vapor phase and has found that the formation of toluene decreases with the total pressure. He suggested that isomerization to toluene occurs not from an electronically-excited molecule of cycloheptatriene but from a vibrationally-excited ground state molecule that is formed by the internal conversion of the electronic energy. Generally speaking, however, a triplet state lies at a lower energy than a singlet state formd from the same orbital, and such large molecules as cycloheptatriene and cyclooctatetraene may easily undergo transitions from the initially-excited singlet to the lower triplet level. Further, in the present case, when an excited mercury atom (^3P) reacts with cycloheptatriene, the triplet-excited molecule is considered to be produced according to the spin conservation rule[8]. Hence, in both cases the isomerization reaction to toluene is likely to arise from the triplet excited molecule. The results in the present experiments are very similar to those obtained by Srinivasan from the direct photolysis at 2600A. Moreover, the value of k_3/k_2 nearly agrees with that calculated from his data[9].

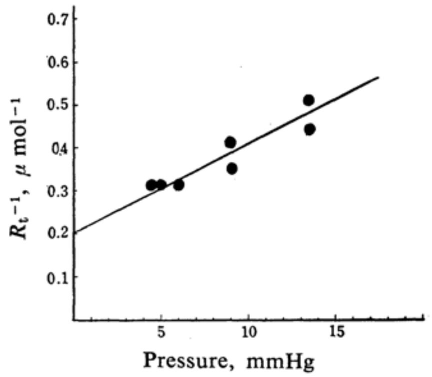

Fig. 4 Relationship between R_t^{-1} and $[C_7H_8]$. R_t is amount of toluene formation for the irradiation time of 30 sec. $[C_7H_8]$ is the pressure of cycloheptatriene.

Srinivasan pointed out that the formation of toluene was not totally quenched by the addition of even considerable amounts of oxygen or nitric oxide. However, it has been reported[10,11] that in the mercury photosensitized reaction of ethylene nitric oxide has no effect on the decomposition reaction of the triplet-excited ethylene. Therefore, the above experimental finding does not necessarily lead to the exclusion of the triplet-excited molecule.

The Electron Spin Resonance of Irradiated Cycloheptatriene[12].—It has been known that when frozen hydrocarbons are irradiated by ionizing radiations, the free radicals produced can be stabilized. A survey of the their ESR spectra gives valuable information concerning the primary act of ionizing radiations. Therefore, we carried out the ESR measurements of electron-irradiated cycloheptatriene frozen at −196°C.

As is shown in Fig. 5, eight equally-spaced lines are observed in the spectrum. This fact clearly indicates that the seven equivalent protons interact on the unpaired electron. That is, the cycloheptatrienyl radical C_7H_7, which has a symmetric conjugated plane frame, is produced by the electron irradiation. On the basis of the simple LCAO MO method, it is to be expected that cycloheptatrienyl radical will have a large delocalization energy, as a

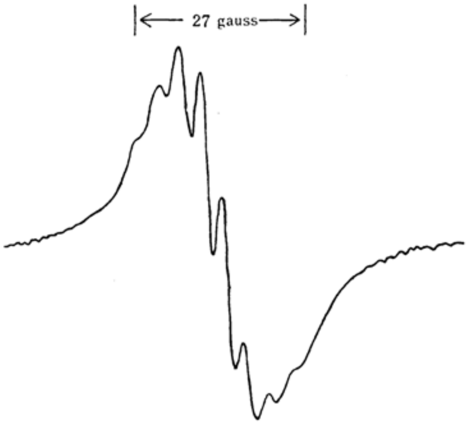

Fig. 5. First derivative ESR spectra of electron irradiated cycloheptatriene. Dose 1×10^8 rad, temperature of irradiation and ESR measurement is −196°C.

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8) K. J. Laidler, "The Chemical Kinetics of Excited States", Oxford University Press, London (1955).

9) He also observed that the formation of toluene at 3130A shows a different pressure dependency from that at 2600A. However, this may be explained as follows. At a shorter wavelength the more vibrationally-excited molecule in the triplet state would be produced as the result of internal conversion. This results in the increase of the rate constant of reaction 2. Consequently, k_3/k_2 at 2600A gets larger than k_2/k_3 at 3130A in Eq. A.

10) S. Arai and S. Shida, *J. Chem. Phys.*, **38**, 694 (1963).

11) D. J. Le Roy and S. W. R. Steacie, ibid., **9**, 839 (1941).

12) S. Arai, S. Shida, K. Yamaguchi and Z. Kuri, ibid., **37**, 1885 (1962).

TABLE I. THE *G* VALUE OF THE PRODUCTS IN THE RADIOLYSIS OF LIQUID CYCLOHEPTATRIENE. Irradiation was made at room temperature. Dose rate was 3900 r/min.

Irradiation time, hr.	Sample g.	*G* Value				Polymer
		H_2 $\times 10^{-2}$	CH_4 $\times 10^{-3}$	C_2H_2 $\times 10^{-3}$	C_2H_4 $\times 10^{-3}$	
24	7.594	5.9	1.6	—	—	3.0
72	3.556	6.8	1.1	—	—	3.2
72	4.805	6.0	1.4	1.6	6.4	3.0
120	5.299	6.2	0.9	3.9	8.6	3.3
120	5.975	7.0	1.2	—	—	3.4
C_8H_8		2.0				0.66

result of which the bond dissociation energy of the parent molecule, $H-C_7H_7$, will be much smaller than the other C–H bonds. Lossing et al.[13] reported 74±7 kcal./mol. for this bond. Generally speaking, in the reaction of radiation chemistry the C–H bonds with lower bond energies are preferentially fractured. This principle leads to the conclusion that the formation of the cycloheptatrienyl radical is one of the major reactions in the radiolysis. In order to obtain a rough estimate of the relative yield of the radical formation, the ESR signal intensity of irradiated cycloheptatriene was compared with that of irradiated benzene under the same experimental conditions. The near equality of the signals shows that cycloheptatriene is as stable as benzene with respect to the radical formation by ionizing radiations. During irradiation and the procedures which followed the sample was open to the air. However, the result with a degassed cycloheptatriene sample was the same as that obtained in air. Therefore, oxygen has no effect on the cycloheptatrienyl radical at −196°C.

The Radiolysis of Liquid Cycloheptatriene.— The *G* value of the products in the radiolysis of liquid cycloheptatriene at room temperature are shown in Table I; they are there also compared with the corresponding values for cyclooctatetraene.

The cycloheptatriene used contained 3 to 5% of toluene as an impurity. Judging from the findings about the irradiation of pure toluene[14], however, the direct effect of radiation on toluene is entirely negligible, even when a maximum is present.

The *G* values of the gaseous products found here are very small. Since cycloheptatriene itself is a reactive scavenger for free radical, those products appear to be produced by a molecular process, a hot atom process being included, or by an ion-molecule reaction. In discussing the radiolytic process, electron impact studies of cycloheptatriene will provide interesting information. In the mass spectra of cycloheptatriene obtained by Meyerson and Rylander[15] the most abundant ion ocurrs at mass 91, and the second most abundant ion, at 92. Other peaks of relative intensity greater than 10% occur at 65 and 39. Accordingly, the following reactions may take place:

$$C_7H_8 + e = C_7H_8^+ + 2e$$

$$C_7H_8 + e = C_7H_7^+ + H + 2e$$

$$C_7H_7^+ = C_5H_5^+ + C_2H_2$$

It is very interesting that the $C_7H_7^+$ ion is produced in a large amount. The results of the ESR experiments show that cycloheptatrienyl radicals are formed by electron irradiation. Juppe et al. suggested a cycloheptatrienyl radical as a precursor of the dimer which was isolated in their experiments. This radical may arise from the recombination of $C_7H_7^+$ with the electron, along with the split of a hydrogen atom from a highly-excited neutral molecule of cycloheptatriene. The formation of the hydrogen molecule may be explained by the abstraction reaction of a hot hydrogen atom, which comes from the energetic fragmentation in these processes. According to Meyerson and Rylander, the cyclic $C_7H_7^+$ ion decomposes into the $C_5H_5^+$ ion and acetylene. Thus, the formation of acetylene may be attributed to this reaction. However, the formation of ethylene can not be explained from the mass spectra of cycloheptatriene, because the ions corresponding to the loss of ethylene from $C_7H_7^+$ and $C_7H_8^+$ are relatively small. Probably in this case more complex reactions take place.

The polymer in Table I contains the C_{14} products, of course, together with the heavier hydrocarbons. Cycloheptatriene has a remarkable reactivity to the radicals, and the polymerization reaction gradually takes place even in the presence of air. Judging from this fact, the *G* value found here may be said

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13) A. G. Harrison, L. R. Honnen, H. J. Dauben and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

14) J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

15) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

to be rather small. That is, the yield of the radical formation in the initial step may be low.

Owing to the presence of toluene in the sample used, the precise G value of the toluene formation was not obtained. However, there was no difference between the gas chromatographic check of toluene before and after irradiation. If the experimental error is taken into account, the G value of toluene will be small, not larger than 0.5.

From these experimental results we concluded that, in the radiation chemistry of liquid cycloheptatriene the major part of the absorbed energy results in the formation of the excited molecule, the electronic energy of which is readily converted to thermal energy. In the case of cyclooctatetraene, its high stability against ionizing radiations was attributed to the collisional deactivation of the excited molecule. The life time of 2×10^{-8} sec. is obtained for the excited cycloheptatriene molecule from the above-mentioned photochemical experiment, assuming that k_3 is about 1×10^{11} l./mol. sec.; that is, every collision leads to deactivation. Consequently, it may be considered that in the liquid phase the excited molecule is deactivated prior to its decomposition or its isomerization.

The over-all reaction mechanism of the radiolysis of cycloheptatriene is:

$$C_7H_8 \rightsquigarrow C_7H_8^*$$

$$C_7H_8^* + C_7H_8 \longrightarrow 2C_7H_8$$

The latter process plays a leading role. In addition,

$$C_7H_8 \rightsquigarrow C_7H_7 + H$$

$$C_7H_8 \rightsquigarrow \mathrm{H(hot)}, C_2H_2, C_7H_7, \text{ etc.}$$

$$\mathrm{H(hot)} + C_7H_8 \longrightarrow H_2 + C_7H_7$$

$$2C_7H_7 \longrightarrow C_{14}H_{14}$$

$$\text{H (or the other radicals)} \xrightarrow{C_7H_8} \text{Polymer}$$

As has been stated above, Juppe et al. found ditropyl as the product in the radiolysis of cycloheptatriene. The other reactions have not been considered here because there is no definite evidence for their occurrences.

Summary

1) In the photosensitized reaction of cycloheptatriene vapor, toluene was produced as the result of isomerization. The amount of toluene formation decreases as the pressure of cycloheptatriene increases. Isomerization to toluene proceeds through the excited molecule, which may be collisionally deactivated.

2) The ESR experiments at low temperatures show that cycloheptatrienyl radicals are formed by electron irradiation. However, the yield of the radical formation is low, nearly equal to that of benzene.

3) In the radiolysis of liquid cycloheptatriene the G values of the gaseous products and toluene are very small. The G value of the polymer seems to suggest the low yield of the radical formation at the initial step. We concluded that the major part of the absorbed energy results in the formation of the excited molecule, the electronic energy of which is readily converted to thermal energy.

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