Mercury Photosensitized Reaction of Cyclo-octatetraene and the Comparison with the Direct Photochemical Reaction

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Both experimental and theoretical investigations on cyclo-octatetraene have been made in our laboratory1-6). Among them the experiment of the direct photochemical reaction3,6), the spectroscopic studies1,4) and the calculation of energy levels2) relate closely to the present work.

Cyclo-octatetraene has two singlet excited states near 2800 Å and 2000 Å1,4), through which the direct photochemical reaction takes place3,6). According to the calculation of the molecular orbitals, however, several triplet states are expected to exist in the vicinity of these singlet states2,7). In view of the spin correlation rule, cyclo-octatetraene may react via the triplet states in the mercury photosensitized reaction8). In order to distinguish between these two processes, the mercury photosensitized reaction has been compared experimentally with the direct photochemical reaction, because even in the latter the reaction mechanism has not yet been clarified in the preceding works3,6). The experiment was carried out in vapor phase in the presence or the absence of mercury vapor, using mercury resonance line, λ2537, under both flow and static conditions, and the preliminary study on the decomposition reactions has already been reported9). In the present study, to elucidate the whole reaction mechanism, decomposition, isomerization and polymerization processes have been investigated quantitatively.

Experimental

Static Method. — The apparatus ordinarily used is shown in Fig. 1. The light source is a quartz mercury resonance lamp wound in the form of a spiral. The lamp was operated from the secondary of a transformer which maintained a current of 100 mA through the lamp and provided a starting potential of 1000 V. In its operation the potential drop across the lamp was 500 V. The lamp emits a small amount of radiation at 1849 Å, which is absorbed by oxygen in the light-path of 15 cm. in length. The light from the lamp was collimated by a quartz lens, in order to make the light nearly parallel at the reaction cell. The absolute light intensity was measured by a uranyl actinometer10), which was placed behind the reaction cell. The light intensity at 2537 Å was approximately 3.7×10^{16} photons/sec.

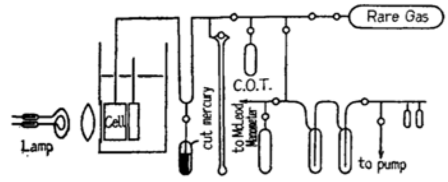

Fig. 1. Apparatus of static system.

Before starting an experiment, the fused-quartz reaction cell (4 cm. long and 5 cm. in diameter) was removed from the system, cleaned with hot chromic acid solution and flamed out. Adding small droplets of distilled mercury, the reaction cell was then attached to the system using de Khotinski cement on the standard taper joint. The de Khotinski cement was chosen because cyclo-octatetraene is insoluble in it. The reaction cell was immersed in a distilled water bath, thermostated at 20.0°C. A definite amount of cyclo-octatetraene vapor was then introduced into the cell and isolated by a mercury cut which served also as a manometer.

At the end of an experiment, the lamp was turned off and the condensable products in the reaction cell were frozen in a trap with liquid nitrogen. The noncondensable gas at dry ice temperature was transferred into a trap with liquid nitrogen through another trap with dry-ice in methanol. After the distillation was completed, the pressure in this part of the system was measured by a small McLeod gauge. The gas mixtures which were noncondensable at dry-ice temperature were analyzed by a mass spectrometer. A Beckman spectrophotometer model

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1) I. Tanaka and S. Shida, This Bulletin, **23**, 54 (1950).

2) Y. Mori, I. Tanaka and S. Shida, ibid., **23**, 168 (1950).

3) I. Tanaka, S. Miyakawa and S. Shida, ibid., **24**, 119 (1951).

4) S. Miyakawa, I. Tanaka and T. Uemura, ibid., **24**, 136 (1951).

5) S. Shida and S. Fujii, ibid., **24**, 173 (1951).

6) I. Tanaka and M. Okuda, *J. Chem. Phys.*, **23**, 1780 (1955).

7) P. Schiess and Mme. A. Pulman, *J. chim. phys.*, **53**, 101 (1956).

8) K. J. Laidler "The Chemical Kinetics of Excited States", Clarendon Press, Oxford (1955), p. 32.

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

10) J. N. Pitts et al., *J. Am. Chem. Soc.*, **77**, 5499 (1955).

D. U. and Hilger E2 type spectrograph were used for the analysis of the products which were condensable at dry-ice temperature.

In the case of the direct photochemical reaction, the absence of mercury vapor has to be fully checked, since the same reaction system is used for those two kind of experiment. The detection of mercury vapor was made by the mercury photosensitized reduction of tungsten oxide in the presence of hydrogen. The greenish tungsten oxide powder turned black for a few minutes of irradiation in the presence of a small amount of mercury vapor. In its absence, however, there was no appreciable change in color even after two hours' irradiation.

In the case of the direct photochemical reaction, oil manometers were used in place of mercury manometers. The small amount of mercury vapor, when left in the system, was trapped with liquid nitrogen. In addition, gold and indium foils, placed in the side tube of the reaction vessel, were used for the removal.

For avoiding the mercury photosensitization, another supplementary experiment was made using the reversed resonance line. The light source was a hot mercury lamp operated by 100 V. D. C. The broadened resonance line was then filtered by a quartz cell containing mercury vapor and hydrogen as quencher.

Flow Method.—The light source was a low-pressure mercury-rare-gas lamp of U-type, which was operated at nearly the same power supply as that for the spiral-type lamp in the static method described before. The dimension of the reaction tube was 20 cm. long and 2.5 cm. in diameter.

In a typical experiment, cyclo-octatetraene was introduced into the reaction system at a linear flow rate, which was controlled by the two cocks placed at both ends of the reaction cell. The cyclo-octatetraene pressure in the reaction tube was measured by a mercury or an oil manometer. During an experiment the product was condensed into the trap immersed in liquid nitrogen. The lamp current was adjusted to a fixed value. At the end of the irradiation, the lamp and the cyclo-octatetraene stream were shut off and the condensable gas in the system was frozen in the trap. The analysis of the products is similar to that in the static method.

Effect of the Addition of Rare Gases.—Since these reactions are supposed to proceed through the excited state of cyclo-octatetraene, the investigation on the deactivation of excited cyclo-octatetraene is of interest. Rare gases are chosen as the quenchers, because of their negligibly small quenching cross section towards the excited mercury atom relative to that of cyclo-octatetraene, and the result is compared with that of ethylene.

The experiment was made in the static system. A definite amount of cyclo-octatetraene was introduced into the reaction cell and condensed with dry-ice. Then a definite amount of the rare gas was added. The system was allowed to stand for four hours for mixing before irradiation. After the reaction was completed the rare gas was gradually pumped off through a trap with liquid nitrogen, in which the acetylene produced was trapped. The amount of acetylene was determined by a method already described. The rare gases which were spectroscopically pure were commercially obtained, and cyclo-octatetraene furnished by the Mitsubishi Kasei Co., was purified by repeating the recrystalization and vacuum distillation.

Result

Decomposition Reaction. — Both in the mercury photosensitized reaction and the direct photochemical reaction, no gas noncondensable at the liquid nitrogen temperature, such as hydrogen and methane, was detected, and the noncondensable at the dry-ice temperature was acetylene. Since acetylene and benzene were produced in the same amount in the mercury photosensitized reaction as well as in the direct photochemical reaction, their appearance seems to be the result of the molecular decomposition. The rate and the quantum yield of the decomposition reaction as a function of cyclo-octatetraene pressure were shown in Fig. 2 and Fig. 3 respectively, in which the rate of the decomposition reaction is that measured by the acetylene produced. In the case of mercury photosensitized reaction, quantum yield of decomposition as a function of cyclo-octatetraene pressure has a maximum; it may be considered that below this pressure the quantum yield decreases on account of the incomplete

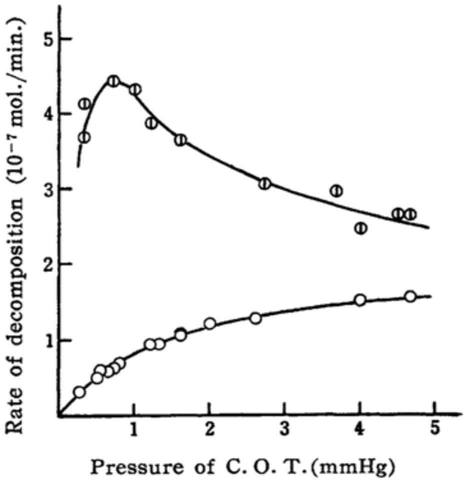

Fig. 2. Rate of decomposition as a function of C.O.T. pressure.
⦶: Mercury photosensitized reaction
○: Direct photochemical reaction

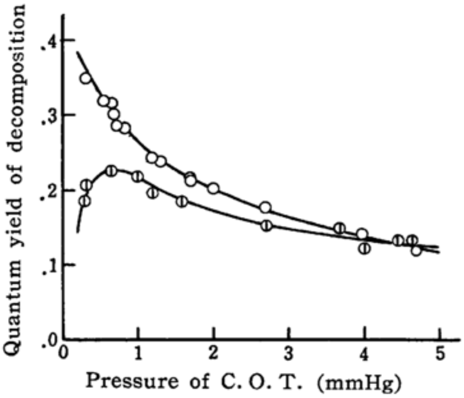

Fig. 3. Quantum yield of decomposition as a function of C. O. T. pressure.
⦶: Mercury photosensitized reaction
○: Direct photochemical reatcion

quenching of the excited mercury atom by cyclo-octatetraene molecule and, above this pressure, the quantum yield also decreases on account of the collisional deactivation of the excited cyclo-octatetraene molecule by the normal cyclo-octatetraene. Such a type of behavior has previously been observed with ethylene. In the case of the direct photochemical reaction, however, the quantum yield of decomposition decreases monotonically as increasing cyclo-octatetraene pressure by the collisional deactivation. Plotting the reciprocal of the quantum yield, ϕ_d, of the decomposition reaction against the pressure of cyclo-octatetraene, straight lines were obtained, which are shown in Fig. 4. From the intercept of the ordinate by these lines, the limiting quantum yield of decomposition can be estimated as 0.3 and 0.4 for the mercury photosensitized reaction and the direct photochemical reaction, respectively.

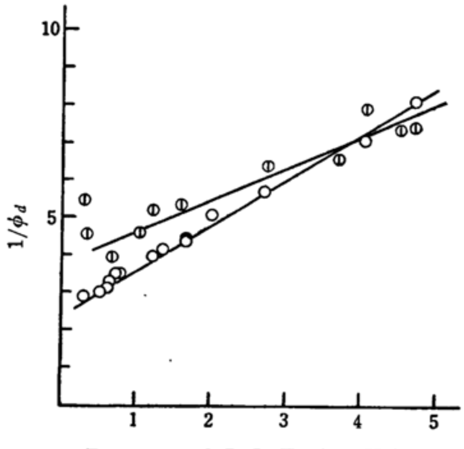

Fig. 4. Plots of $1/\phi_d$ as a function of C. O. T. pressure.
⦶: Mercury photosensitized reaction
○: Direct photochemical reaction

In the experiment with the reversed light source, the rate of the decomposition reaction as a function of pressure of cyclo-octatetraene is shown in Fig. 5. This is similar to the result in the direct photochemical reaction in absence of mercury vapor.

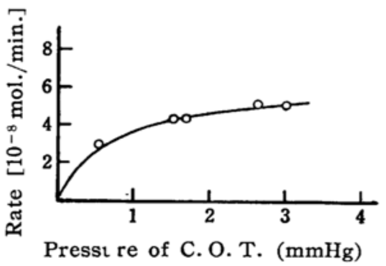

Fig. 5. Rate of decomposition as a function of C. O. T. pressure.
(A filter containing mercury vapor and hydrogen gas was used.)

Polymerization and Isomerization Reaction.—As the reaction proceeds, a thin yellowish film deposits in front of the reaction cell, which seems to owe to the polymerization of cycro-octatetraene. To examine the polymerization reaction, the total pressure change and the amount of acetylene produced were measured in the course of reaction in the complete quenching region of cyclo-octatetraene pressure for the excited mercury atom. The result of the experiment was shown in Fig.

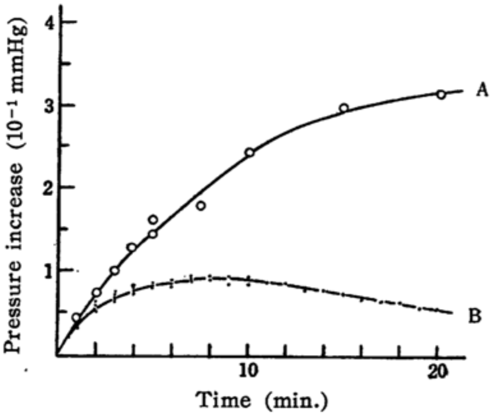

Fig. 6. Total pressure increase and acetylene production in the course of reaction.
A: Acetylene production
B: Total pressure change

6, in which the total pressure initially increased, reaching a maximum after about seven minutes' irradiation and then began to decrease slowly; the production of acetylene on the other hand increased monotonically except that the rate of production gradually decreased on account of the filtering effect by the polymeric clinging to the front of the reaction cell. In this experiment the amount of acetylene produced was measured after the reaction was complete in each run. By removing acetylene produced, no change was observed in the behavior of the total pressure variation in the course of the reaction. Therefore it may be considered that acetylene does not act as an intermediate of the polymerization reaction and furthermore the secondary effect of acetylene is ignored in this reaction. After irradiation, absorption spectra of the mixture of reaction products and cyclo-octatetraene were measured in methanol solution. The result was shown in Fig. 7, in which there is seen a marked increase in absorption spectra at the wave length near 2900 Å. The product shows orange color due to the fact that the foot of this absorption is in a visible region. This absorption spectrum shows also the band structure at 3050, 3005, 2912 and 2820 Å in the gas phase spectrogram. The absorption spectra gradually increased and reached a maximum value after about seven minutes' irradiation as observed for the total pressure change in Fig. 6.

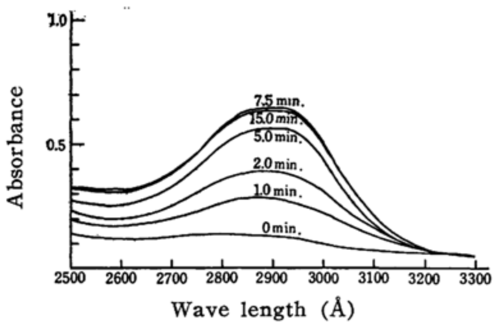

Fig. 7. Change of absorption spectrum in the course of reaction.

The spectra of unirradiated cyclo-octatetraene, that obtained after 20 minutes' irradiation and that preserved for a week in vacuo are shown together in Fig. 8. The orange colored liquid, which seems to be an isomer of cyclo-octatetraene, is unstable and during the presservation in vacuo for a week, a yellowish plastic substance was obtained which is partially soluble in hexane and shows an absorption near 2600 Å. In this polymerizing process there is no evidence that non-condensable gases in dry-ice temperature such as acetylene and hydrogen are produced. The orange colored liquid may be polymerized without decomposition.

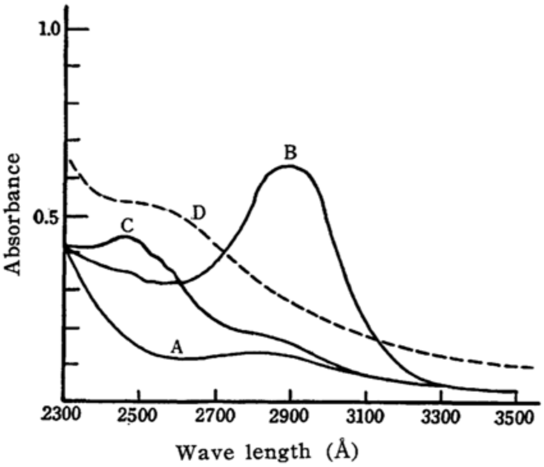

Fig. 8. A: Before the run. B: After the run. C: After the run and a week stored in vacuo. D: Polymer film dipositted in front of the reaction cell.

In an attempt to examine the initial stage of the reaction just described more precisely, a series of runs was made under the flow condition. The relative amount of the orange-colored liquid produced was measured by the absorption at 5000 Å using the pure cyclo-octatetraene as the reference. An experiment has been made on the pressure dependence of the production of orange-colored liquid in comparison with that of acetylene production, only in the mercury photosensitized reaction. The result, as shown in

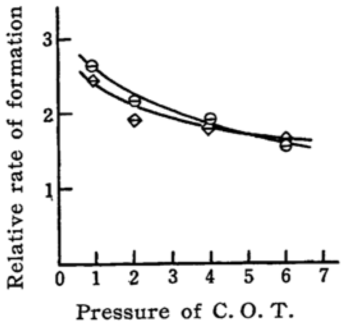

Fig. 9. Relative rate of production of acetylene and orange-colored substance in mercury photosensitized reaction. ⊖ Acetylene ◈ Orange-colored substance (Different scales were used for two kinds of products).

Fig. 9, almost coincides with that of acetylene production.

The relative amount of acetylene and orange-colored liquid has been investigated both in the mercury photosensitized reaction and the direct photochemical reaction. The plots against the time of the relative amount of these products were shown in Fig. 10. The ratio of the production of orange-colored liquid to that of acetylene is twice as great in the photosensitized reaction as in the direct photochemical reaction. Assuming the extinction coefficient of the orange-colored liquid at 2900 Å as 10^4, the ratio of orange-colored liquid to acetylene is about 2:1 and 1:1 in the mercury photosensitized reaction and the direct photochemical reaction, respectively. In the forgoing experiment, as the limiting quantum yield of decomposition was 0.3 and 0.4 for the mercury photosensitized reaction and the direct photochemical reaction, respectively, it may be considered that the whole excited cyclo-octatetraene molecules would undergo either the decomposition reaction or the isomerization giving orange-colored liquid in the limiting case in which the pressure of cyclo-octatetraene is zero.

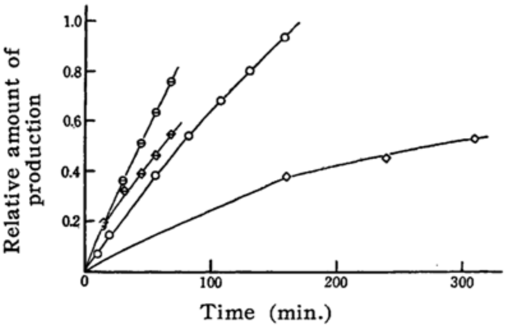

Fig. 10. Relative amounts of production of acetylene and orange-colored substance. ⊖ Acetylene ◈ Orange-colored substance (mercury photosensitized reaction); ○ Acetylene ◇ Orange-colored substance (direct photochemical reaction) (different scales were used for two kinds of products).

Styrene Formation.—In the case of the mercury photosensitized reaction, for over 20 minutes' irradiation, new absorption spectral lines at 2800 Å and 2880 Å appeared in the gas phase spectrogram of the reaction products, which coincide with that of styrene. The amount of styrene produced was about one-tenth of benzene and therefore we performed no further quantitative experiment on this product, because this seems to make little contribution to the elucidation of the reaction mechanism.

Effect of the Addition of Rare Gases.—As shown in Fig. 2 and Fig. 9, the rate of the decomposition reaction and that of the formation of orange-colored liquid decrease with increase in the pressure of cyclo-octatetraene. Then it may be considered that the excited cyclo-octatetraene molecule is deactivated by cyclo-octatetraene itself. The collisional deactivation of excited cyclo-octatetraene was also investigated, measuring the change in the quantum yield of the decomposition reaction by mixing rare gases.

The reciprocal of the quantum yield of decomposition measured by the amount of acetylene produced is plotted against the pressure of rare gases in Fig. 11, in which there is seen a fairly well linear relationship between these two quantities.

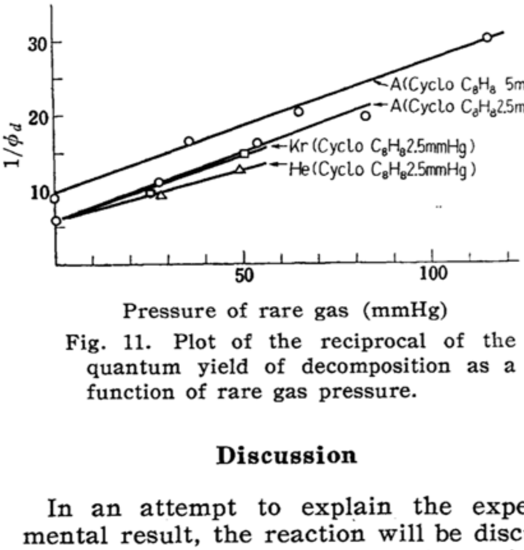

Fig. 11. Plot of the reciprocal of the quantum yield of decomposition as a function of rare gas pressure.

Discussion

In an attempt to explain the experimental result, the reaction will be discussed in terms of a sequence of reactions which is somewhat similar to the one proposed for ethylene; however, in addition the discussion includes the reactions producing orange-colored liquid (presumably bicyclo form of C_8H_8) and polymer. The reaction mechanism is as follows:

$$\mathrm{Hg} + h\nu \rightarrow \mathrm{Hg}^* \qquad \text{(a)}$$

$$\mathrm{Hg}^* \rightarrow \mathrm{Hg} + h\nu \qquad \text{(b)}$$

$$C_8H_8 + \mathrm{Hg}^* \rightarrow C_8H_8^*(\text{triplet}) + \mathrm{Hg} \qquad (1)$$

$$C_8H_8^*(\text{triplet}) + C_8H_8 \rightarrow 2C_8H_8 \qquad (2)$$

$$C_8H_8^*(\text{triplet}) \rightarrow C_2H_2 + C_6H_6 \qquad (3)$$

$$C_8H_8^*(\text{triplet}) \rightarrow \text{bicyclo } C_8H_8 \qquad (4)$$

$$\text{bicyclo } C_8H_8 + Hg^* \rightarrow \text{bicyclo } C_8H_8^* + Hg \qquad (5)$$

$$\text{bicyclo } C_8H_8^* + \text{wall} \rightarrow \text{polymer} \qquad (6)$$

For the direct photochemical reaction in place of step 1 the following two processes may be considered,

$$C_8H_8 + h\nu \rightarrow C_8H_8^*(\text{singlet}) \qquad (1a)$$

$$C_8H_8^*(\text{singlet}) \rightarrow C_8H_8^*(\text{triplet}) \qquad (1b)$$

Even in the case of mercury photosensitized reaction, it will be possible for the direct light absorption by cyclo-octatetraene molecules to occur. The absorption coefficient of mercury vapor at room temperature for mercury resonance line is about 3 cm.$^{-1}$ [11], while the absorption coefficient for several mmHg of cyclo-octatetraene is 0.1 cm.$^{-1}$, the extinction coefficient of the latter at 2537 Å being 300 l./mol. cm.[1,4] Hence the mercury resonance line was selectively absorbed by mercury vapor under the condition studied; the reaction 1a will be ignored in comparison with reaction 1.

Making use of the usual stationaly state assumption, we find the concentration of of Hg* and C_8H_8* to be

$$[C_8H_8^*] = k_1[C_8H_8][Hg^*]/(k_2[C_8H_8] + k_3 + k_4) \qquad (1)$$

$$[Hg^*] = I_{\text{abs}}/(k_b + k_1[C_8H_8]) \qquad (2)$$

The rate of acetylene production is given by

$$d[C_2H_2]/dt = k_3[C_8H_8^*] \qquad (3)$$

Eqs. 1 and 2 are introduced into Eq. 3 to give the quantum yield of decomposition, ϕ_d, as a function of cyclo-octatetraene,

$$\phi_d = k_1k_3[C_8H_8]/(k_1[C_8H_8] + k_b)(k_2[C_8H_8] + k_3 + k_5) \qquad (4)$$

Similarly in the case of the direct photochemical reaction we have.

$$\phi_d{}' = k_3{}'/(k_2{}'[C_8H_8] + k_3{}' + k_4{}') \qquad (5)$$

The pressure dependence of the quantum yield of the decomposition can be interpreted by the formulae 4 and 5 in the pressure range studied; thus in the mercury photosensitized reaction the quantum yield of decomposition has a maximum, while in the case of the direct photochemical reaction the quantum yield of decomposition monotonically decreases as cyclo-octatetraene pressure increases.

The reaction rate constants in the sequence of reactions can be estimated from the formulae mentioned above: k_b, the reciprocal of the life time of the excited mercury atom, Hg(6^3P_1), is 10^7 sec.$^{-1}$ [12], and from the slope of the straight line in Fig. 4 the value of k_2/k_3 is 2.1×10^7 cc./mol., and as we have described (Result, polymerization and isomerization reaction) k_3/k_4, the ratio of formation of acetylene to the orange-colored liquid, is 0.5. If the excited cyclo-octatetraene molecule is deactivated by one collision with the normal cyclo-octatetraene molecule, then assuming the collisional diameter as 6 Å, the life time of the excited cyclo-octatetraene molecule is calculated to be 10^{-8} sec.

Similarly in the case of the direct photochemical reaction the ratio of the reaction constants can be estimated from Fig. 4 as $k_2{}'/k_3{}' = 2.5 \times 10^7$ cc./mol. and $k_3{}'/k_4{}' = 1$, which is the same order of magnitude as those of the mercury photosensitized reaction.

Differentiating Eq. 4 with respect to $[C_8H_8]$ and putting it to be zero, then the following expression is obtained:

$$k_1 = (k_3 + k_4)k_b/k_2P_0^2 \qquad (6)$$

where P_0 is the pressure of cyclo-octatetraene corresponding to the maximum ϕ_d.

Introducing the reaction rate constants estimated before into Eq. 6, k_1 becomes 10^{15} cc./sec. mol., from which the quenching cross section of the excited mercury atom by cyclo-octatetraene is to be 10^2 Å^2, which is of reasonable magnitude.

The collisional deactivation of the excited cyclo-octatetraene molecule may be explained by the following reaction in addition to the above sequence,

$$C_8H_8^*(\text{triplet}) + M \rightarrow C_8H_8 + M \qquad (7)$$

where M is rare gas.

The quantum yield of decomposition is then represented by the following equation,

$$\phi_d = k_1k_3[C_8H_8]/(k_1[C_8H_8] + k_b) \times (k_2[C_8H_8] + k_7[M] + k_3 + k_4) \qquad (7)$$

which can be reduced, under the condition for the complete quenching of the excited mercury atom, to

$$\phi_d{}^{-1} = k_7[M]/k_3 + \text{const.} \qquad (8)$$

The relative efficiencies of deactivation calculated from the slope of the lines in Fig. 11 are 0.13, 0.19 and 0.17 for helium, argon and krypton respectively, taking the efficiency of cyclo-octatetraene as unity.

The deactivation cross section calculated

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[11] A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms", Cambridge Univ. Press, Cambridge (1934) p. 203.

[12] see reference 11) p. 147.

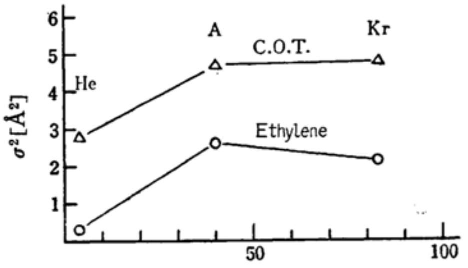

Fig. 12. Quenching cross section of excited C. O. T. and ethylene molecule by rare gases.

from these values were shown in Fig. 12 together with those of ethylene[13], where the cross section for self-deactivation were taken as 30 Å^2 and 11 Å^2 for cyclo-octatetraene and ethylene respectively by considering the geometrical dimension. There is seen a parallel dependence of the cross section on the molecular weight of the deactivating gases.

The estimation of the rate constants can also be made on the isomerization and the polymerization path,

$$\begin{aligned} &\mathrm{d}[\text{bicyclo } C_8H_8]/\mathrm{d}t \\ &= k_4[C_8H_8^*] - k_5[\text{bicyclo } C_8H_8][Hg^*] \\ &= k_1k_4[C_8H_8][Hg^*]/(k_2[C_8H_8]+k_3+k_4) \\ &\qquad - k_5[\text{bicyclo } C_8H_8][Hg^*] \end{aligned} \tag{9}$$

Integrating Eq. 9 [bicyclo C_8H_8] is given as a function of time:

$$[\text{bicyclo } C_8H_8] = A\{1-\exp(-Bt)\} \tag{10}$$

where the constants A and B are given by

$$A = k_1k_4[C_8H_8]/k_5(k_2[C_8H_8]+k_3+k_4) \tag{11}$$

and

$$B = k_5I_{\text{abs}}/(k_1[C_8H_8]+k_b) \tag{12}$$

For the formation of the polymer, the following equation will be obtained,

$$\mathrm{d}[P]/\mathrm{d}t = k_5[\text{bicyclo } C_8H_8][Hg^*] \tag{13}$$

Integrating the equation, the amount of polymer produced is given by

$$[P] = ABt + A\{\exp(-Bt)-1\} \tag{14}$$

The experimental result shown in Fig. 7, that the amount of orange-colored liquid increases reaching a saturation value after seven minutes' irradiation, may be explained by the formula 10. Using this formula the parameter was estimated as follows; B is 5×10^{-2} sec.$^{-1}$, then k_5 calculated from Eq. 12, is 10^{14} cc./mol. sec. which is a reasonable value considering that the polymerization proceeds with a small amount of activation energy.

In Fig. 6, if we consider that the difference between the production of acetylene and the total pressure-increase is equal to the production of polymer, then the rate of production is zero at the beginning of the irradiation and becomes constant after a sufficient time later. This trend of polymer production can be quantitatively explained by Eq. 14.

The electronic states of mercury atom and cyclo-octatetraene molecule are shown in Fig. 13, in which the singlet states are inferred from the spectroscopic data[1,4]. For the triplet states, the values from the molecular orbital calculation were used because of lack of the experimental data[2,7]. Some ambiguity is involved, however, in the determination of the assignment of those states.

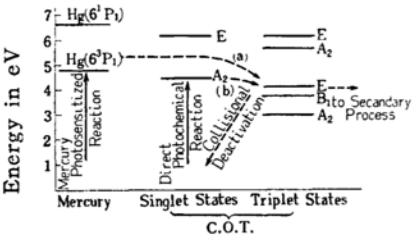

Fig. 13. Electronic states of mercury and C. O. T.

In the case of the mercury photosensitized reaction, it may be considered that the reaction proceeds by path a); on the other hand in the case of the direct photochemical reaction, by path b). From the similarity of the reaction products and of the quantum yield, it may be considered that there is a cross between these states through which the reaction takes place.

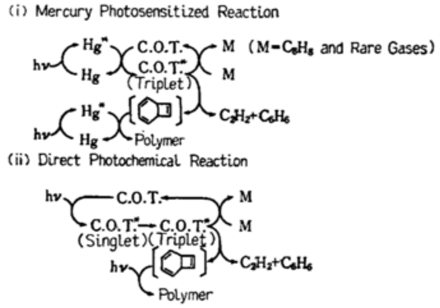

Fig. 14. Schematic representation of the mercury photosensitized and direct photochemical reactions of cyclo-octatetraene.

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[13] A. B. Callear and J. C. Robb, *Discussion Faraday Soc.*, No. **17**, 21 (1954).

The whole process of the reactions, mercury photosensitized as well as direct photochemical, are schematically represented in Fig. 14. Both the reactions involve the same kinds of process, i. e. the excitation of cyclo-octatetraene, the deactivation and the decomposition of the excited cyclo-octatetraene, and the polymerization process through the orange-colored liquid as intermediate.

Although the bicyclo form as an isomer of cyclo-octatetraene has not been isolated, the bicyclo forms of several derivatives of cyclo-octatetraene show ultraviolet spectra similar to those of the present orange-colored liquid[14], and this variation has been used by Reppe as an intermediate of the reaction of cyclo-octatetraene[15].

Further discussion on the present problem, however, would be largely speculative and would require much more detailed experimental result.

Summary

The reaction products of both the mercury photosensitized reaction and the direct photochemical reaction are the same, i. e. acetylene, benzene, orange-colored liquid (presumably bicyclo form of C_8H_8), polymer and a trace of styrene; the non-condensable products at liquid nitrogen temperature such as hydrogen and methane were not detected.

A quantitative experiment has been made on the decomposition reaction, in which cyclo-octatetraene shows a similar behavior to ethylene in the pressure dependence of the quantum yield. The quantum yields of the decomposition are of the same magnitude in both the mercury photosensitized and the direct photochemical reaction. The result shows that the two reactions proceed via the same excited state (probably triplet), directly or indirectly.

An investigation has also been made on the polymerization reaction, for which the total pressure change and the absorption spectrum of the reaction products have been examined in the course of the reaction. It is concluded that the polymerization takes the place via orange-colored liquid as an intermediate.

In the study of the reaction of hydrocarbons with $Hg(6^3P_1)$ atom a great deal of evidence has now been accumulated which shows the fact that the reaction always accompanies hydrogen production. The mercury photosensitized reaction of cyclo-octatetraene is one of the rare exceptions in this generality.

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