The Photochemical Reaction of Cycloöctatetraene (C_8H_8)

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Introduction

The properties of cycloöctatetraene (C. O. T.) have been lately investigated by several physicochemical methods. We have calculated the energy levels of C. O. T. as the symmetry of D_{2d},(1) D_4,(2) and D_{4d}(3) by the HLSP method(4) and the GMS method,(5) and then its electronic structure has been discussed in comparison with the experimental results of thermochemical data(6), magnetic susceptibility(7) and absorption spectra.(8)

We have newly found that C. O. T. undergoes the photochemical reactions by the mercury vapor lamp. Hence, C. O. T. was excited by mercury lamp and the gaseous products were examined by their absorption spectra. The quantum yield for benzene in the product was spectrographically determined, and the increase in the pressure of non-condensable producing gas was measured by a Bourdon gauge. The purpose of the present paper is to report these experimental results.

Electronic Structure of C. O. T.

The energy levels of C. O. T. was calculated as the most probable symmetry of D_{2d} by the HLSP method and the GMS method and are shown in Fig. 1. The absorption band below 2000 Å. was ascribed to the $^1A_1 \rightarrow {}^1E$ transition and the shoulder at 2800 Å. of the absorption band of longer wave length to the $^1A_1 \rightarrow {}^1A_1$ or $^1A_1 \rightarrow {}^1A_2$ transition. The levels which are calculated by the HLSP method for non-polar structures do not include the $^1A_2$ level. But the $^1A_2$ level appears in the calculation when it is only polar structures. The wave length of the transition $^1A_1 \rightarrow {}^1A_2$ is calculated to be shorter than 2000 Å. according to Craig's estimation.(9) But it is of interest as the property of approximate calculations that the levels appear on the lower or upper side; the molecular orbital introduces extra polar structures like GMS methods and makes the energy $^1A_2$ lower, while the atomic orbital raises the level $^1A_2$ made of polar structures.

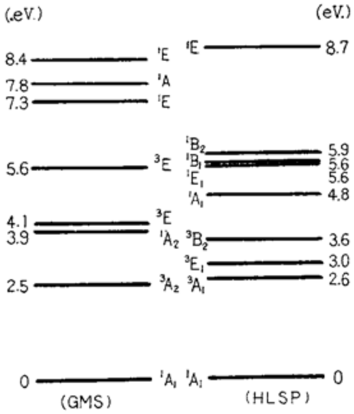

Fig. 1.

There are some recent investigations about the interaction in the systems consisting of I_2 and aromatic compounds, especially benzene.(10) The following results were recognized from the relation obtained in the systems of I_2 and C_8H_8,(11) namely, the absorption band at 2800 Å. for C_8H_8 (CCl_4 solution + I_2) has the order of $\varepsilon = 450$, which is about twice as large as that of heptane solution ($\varepsilon = 250$), but does not

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(1) H. S. Kaufmann, I. Fankuchen and H. Mark, *J. Chem. Phys.* **15**, 414 (1947); H. S. Kaufmann, I. Fankuchen and H. Mark, *Nature*, **161**, 165 (1948); K. Hedberg and V. Schomaker, Annual Meeting of Am. Chem. Soc., 1949.

(2) E. P. Lippincott, R. C. Lord and R. S. MacDonald, *J. Chem. Phys.* **16**, 548 (1948); E. P. Lippincott, R. C. Lord and R. S. MacDonald, *Nature*, **166**, 227 (1950); O. Bastiaisen and O. Hassel, Acta Scandinavica, **3**, 209 (1949).

(3) O. Bastiaisen, O. Hassel and A. Langseth, *Nature*, **160**, 128 (1947); B. D. Saksena and H. Narain, *Nature*, **165**, 723 (1950).

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

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

(6) D. W. Scott, M. E. Gross, G. D. Oliver and H. M. Huffmann, *J. Am. Chem. Soc.*, **71**, 1634 (1949); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **69**, 2068 (1947); E. J. Prosen, W. H. Johnson and F. D. Rossini, *J. Am. Chem. Soc.* **72**, 626 (1950); J. L. Cotrell and L. E. Sutton, *J. Chem. Phys.* **15**, 685 (1947).

(7) R. C. Pink and A. R. Ubbelohde, *Nature*, **160**, 502 (1947); R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948); F. R. M. MacDonnell, R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **46**, 156 (1950); S. Shida and S. Fujii, Annual Meeting of Chem. Soc. Japan, 1950.

(8) A. Langseth and S. Broderson, *Acta Chemica Scandinavica*, **3**, 778 (1949); S. Miyakawa, I. Tanaka and T. Uémura, in process of publication.

(9) D. P. Craig, Proc. Roy. Soc., **A 200**, 272, 390, 401 (1950).

(10) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71** 2703 (1949); R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

(11) unpulished.

increase more than fifty times as in the case of benzene. So it is concluded that the electronic structure of C. O. T., though it being a ring compound, is different from those of the aromatic compounds. This conclusion coincides with the experimental results of the previous reference papers.(1)~(8), (12)

The Photochemical Reactions, Experimental

The sample of C. O. T. was prepared by Prof. S. Murahashi and Dr. N. Hagiwara in the Institute of Scientific and Industrial Research, University of Osaka and was used in our experiments. The C. O. T. was purified by four time fractional distillations in vacuum in which the more volatile and the heavier portions were discarded.

The experimental arrangement is shown in Fig. 2. The low pressure mercury arc was set against the cylindrical quartz tubes (reaction cell) of different lengths, where the gaseous C. O. T. was introduced by distillation from the sample tube at room temperature. The photochemical reactions of C. O. T. in the cell were carried out by light which passed a filter between the cell and the arc. On the other hand, another cell with plane quartz windows was set between Jobin-Yvon spectrograph and the hydrogen discharge tube that was connected with the first cell so that the gaseous C. O. T. and its products diffuse into the cell. Their absorption spectra could thus be obtained.

The quantum yield of the reaction where C. O. T. is decomposed into benzene was determined using the uranyl sulfate and oxalic acid as actinometer. Corrections were made for light reflection on quartz-air interfaces.

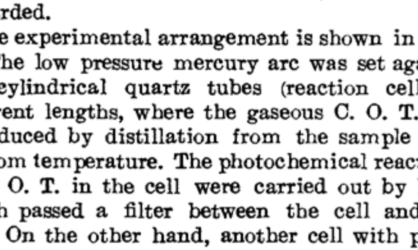

Fig. 2.—M, manometer; H, hydrogen discharge tube; C_1 and C_2, cell; Sp, spectrograph; S, sample; F, filter; and Hg, mercury lamp.

We have found the benzene as a product, hence the following process can be considered, $C_8H_8 + h\nu \rightarrow C_6H_6 + C_2H_2$. If this mechanism is true, it is expected that the pressure should increase as a result of the formation of C_2H_2, non-condensed at low temperature. In order to ascertain this consideration, a cylindrical quartz cell of 20 cc. capacity was connected directly to a gauge of the Bourdon type and the pressure change of non-condensable gas can be read with a cathetometer.

These experiments were carried out in the pressure range from 2 to 7 mm.Hg. of C. O. T.. For the filter, glass (above 3300 Å.), P. V. A. (above 2300 Å.), etc. were used.

Results and Discussions

First of all, the results which were qualitatively observed by the absorption spectra of photochemical products of C. O. T. are shown as follows. The characteristic absorption bands of benzene (2610 Å., 2550 Å., 2480 Å., 2420 Å., ...) were observed in the spectra which could be obtained through the second cell of 50 to 95 mm. length, by illumination of mercury arc, for 10 to 60 minutes. In order to find other substances but benzene, by using the second cell of 200 mm. length, narrowing the slit and operating the mercury arc for 1 to 3 hours, new absorption bands which were not recognized in the case of the shorter cell, could be found at 2916 Å. (s), 2916 Å.∼2885 Å (diffuse), 2885 Å. (s), 2877 Å. (w), 2872 Å. (w), 2840 Å. ∼2700 Å. (diffuse), 2816 Å. (w) and 2800 Å. (w) (where the notation s means strong and w weak intensity).

In order to study what substances have given these absorption bands, the absorption spectra of pure gaseous styrene were taken. Its strong absorptions at 2885 Å., 2877 Å., 2872 Å., 2816 Å. and 2800 Å. could be confirmed to coincide with the above-mentioned bands, so we can conclude that the styrene, an isomer of C. O. T., is also produced in the photochemical reaction of C. O. T. We can not yet determine from which of reacting substances come those bands at 2916 Å. (s), 2916 Å.∼2885 Å. (diffuse band) and 2840 Å.∼2700 Å. (diffuse band) which are not observed in the spectra of styrene. We may, however, suppose that these bands may be dependent on some compounds like C. O. T. which contain some conjugated double bonds, since these substances will have absorption bands of longer wave lengths than 2000 Å. In order to determine whether benzene can be directly produced by the photodecomposition of C. O. T. or by the photodecomposition of styrene that is produced by the isomerization of C. O. T., the reaction products, which were produced from pure styrene in gaseous phase by the mercury lamp at the same condition as the case of the photoreaction of C. O. T., can be studied their absorption spectra. The reactions by the illuminations for 10 min., 30 min., and 60 min. gave no benzene at all, and

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(12) Cf. R. M. Elofson, *Anal. Chem.*, **21**. 917 (1949).

the intensity of the absorption spectra of styrene was only decreased. This fact is probably due to the photopolymerization of styrene. So that, we can ascertain that the photodecomposition to benzene is the direct one.⁽¹³⁾

If we compare the absorption spectra which were obtained in 200 mm. cell for the resultant of the photochemical reaction and the spectra that were respectively obtained from pure styrene in various pressures, we can recognize that the quantity of reaction of photodecomposing to benzene is larger than that of isomerizing to styrene, although this conclusion is not certain, because the styrene changes to polystyrene in small quantity.

It may be considered that the reason why the photodecomposition of C. O. T. to benzene is easier than the isomerization of C. O. T. to styrene is that after the excitation by photon the breaking of the single bonds (=CH–CH=) is easier than the displacement of the hydrogen atom.⁽¹⁴⁾

Next, to investigate the reaction $C_8H_8+h\nu\rightarrow C_6H_6+C_2H_2$, the results that are obtained for the non-condensable gas at low temperature will be illustrated. A trap which is prepared between the cylindrical quartz cell (20 cc.) and Bourdon Gauge, can be cooled after the exposition of the cell to light, in alcohol with dry ice to condense out C. O. T., benzene, styrene, and etc., and the pressure of non-condensable gas could be measured. The initial pressure of C. O. T. was 2.50 to 3.50 mm.Hg. An example is shown in Table 1.

Table 1

The initial pressure of C. O. T., mm.Hg	Filter	Pressure of non-condensable gas, mm.Hg		
		10 min.	30 min.	60 min.
2.60	None	0.06	0.14	0.25
2.92	P. V. A.	—	0.04	0.06
3.32	Glass	0	0	0

Conditions of above reaction: The cell is set parallel to mercury arc. (100 V., 5 Amp.) Temp. 25°.

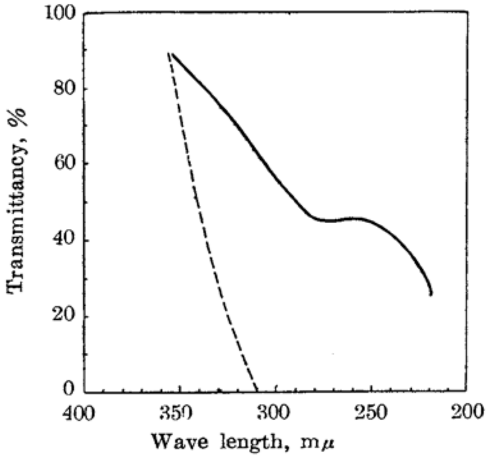

Fig. 3.—Transmission of the filters: ——, PVA-filter; - - -, glass.

The measured values of transmissions of the filters used are shown in Fig. 3. According to these results that are given in Table 1, it is clear that besides C_6H_6 a non-condensable gas, probably C_2H_2, is produced by the photochemical reaction. When the light below 3300 Å. was cut off by glass, C. O. T. did not decompose photochemically as well as the results of quantum yield of C_6H_6 as stated later will show. By comparing the reactions with and without filter P. V. A. it is clear that the light below 2500 Å is important for the photochemical decomposition.

Next, the quantum yield of reaction in which C. O. T. decomposes to benzene will be stated. The experimental arrangements are shown in Fig. 2.

In order to determine the quantity of benzene which is produced in the photochemical reaction, the extinction of pure benzene was first measured in various pressures by the microphotometry of the absorption spectra of gaseous benzene that were distilled three times in vacuum. The benzene which is produced by photochemical reaction in various conditions could be quantiatively determined. On the other hand, when we can measure the fraction of light that was absorbed by chemical actinometer, the quantum yield may be determined. An example of the experimental data is written in Table 2.

Table 2

The Photodecomposition of C. O. T. at 25°.

The initial pressure of C. O. T., mm. Hg	Filter	Pressure of benzene produced, mm. Hg		
		10 min.	30 min.	60 min.
5.0	None	0.18	0.47	0.70
5.0	P. V. A.	—	0.13	0.23
5.0	Glass	0	0	0

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(13) B. L. Dunicz, *J. Am. Chem. Soc.*, **63**, 2461 (1941). It was reported that the characteristic bands of styrene was not found in the course of the photochemical reaction in acetylene-benzene mixture for irradiation. The authors are indebted to Z. Kuri for valuable discussions about this experiment.

(14) Norrish, *Trans. Faraday* Soc., **30**, 103 (1934); Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935); The interesting facts for shift of hydrogen atom about the photodecomposition of cycloketones were reported.

From the data of actinometry with uranyl sulfate and oxalic acid, the absorbed quanta are 5.1×10^{18} and the decomposed molecules are 0.41×10^{18} in a half hour. Then the quantum yield for decomposition to benzene is about 0.1 for light near 2537 Å. It is also seen in Table 2 that the light which is shorter than 2500 Å. is important for the photochemical decomposition, as we have already mentioned. The absorption bands below 2500 Å. can be considered as due to the $^1A_1\rightarrow{}^1E$ transition which was given by the calculation for the electronic structure of C. O. T. A configuration of a polyatomic molecule for an electronic state having orbital degeneracy can not be stable with respect to all displacements of the nuclei (Jahn-Teller effect).(15) We can suppose that the Jahn-Teller effect will be very small in benzene, even if it occurs, as π-electrons have less contribution to the chemical binding than σ-electrons, then the decomposition is impossible by mercury lamp.(16) We may consider that C. O. T. is not stable through the change of the shape of molecule as the Jahn-Teller effect is more effective for C. O. T. than for benzene and C. O. T. will be decomposed by light which has shorter wave length than 3000 Å.

Summary

By the absorption spectra, it was found that benzene and styrene were independently produced from C. O. T. when C. O. T. was excited by the light shorter than 3000 Å., and that some unknown substances giving a sharp line at 2916 Å. and two diffuse bands at 2916 Å.$\sim$2885 Å. and 2840 Å.$\sim$2700 Å. were also produced. The gas like acetylene which can not be condensed by dry ice can be at the same time produced.

The quantum yield of reaction where C. O. T. is decomposed to benzene by light near 2537 Å. was about 0.1. And the light which has the shorter wave length than 2500 Å. mainly contributes to the reaction in which C. O. T. decomposes to benzene.

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(15) H. A. Jahn and E. Teller, *Proc. Roy. Soc.*, A **161**, 220 (1937); H. A. Jahn, *ibid.*, A **164**, 117 (1938).

(16) Kistiakowsky and Solomon, *J. Chem. Phys.* **5**, 609 (1937).