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The Photolysis of 1,3-Cyclootadiene Vapor. Vibrationally Excited Molecules Produced by the Photoelimination of Ethylene

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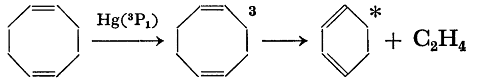
Photochemical initiation has often been used as a method of studying vibrationally-excited molecules.[1] The primary step in many systems is followed by a sequence of steps, which may include conventional unimolecular processes of species with excess energy. In a previous paper of this series,[2] it has been observed that a vibrationally-excited molecule (**1**) was produced by the elimination of ethylene in the mercury-photosensitized decomposition of 1,5-cyclooctadiene (1,5-COD) vapor:



(**1**)

The vibrationally-excited molecule (**1**) may decompose to benzene and hydrogen, may be collisionally stabilized to 1,3-cyclohexadiene(CHD), or may isomerize to 1,3,5-hexatriene(HT). In the present study, it has been observed that the mercury-photosensitized decomposition of 1,3-cyclooctadiene (1,3-COD) also causes an elimination of ethylene, leading to the formation of a vibrationally-excited 1,3,5-hexatriene molecule which gives final products similar to those from 1,5-COD.

Experimental

The experimental procedures were essentially the same as those reported previously in the photolysis of 1,5-COD.[2] The vapor of 1,3-COD, which had been obtained commercially and which had been shown to be 99.8% pure by gas-chromatographic analysis, was irradiated in a quartz reaction vessel (5-cm in diameter and 5 cm long) with light from a low-pressure mercury resonance lamp in the presence of a small amount of mercury vapor. Most of the runs were at temperatures between 20 and 22°C.

The product gases volatile at −196°C were collected by means of a Toepler pump in a gas buret in a greaseless vacuum system, and then subjected to a Pd thimble heated at 300°C for hydrogen measurements. The other products were analyzed mainly gas chromatographically. A 3-m silica gel column at 100°C was used for the gases volatile at −120°C (C_2 fraction), and a 7.5-m squalane column at 80°C was used for the liquid components. Quantitative determinations were based on the calibrations of peak areas using measured amounts of certain hydrocarbon standards (propane and benzene respectively).

The quantum yields were determined by comparison with those of the mercury-photosensitized decomposition of propane at 300 mmHg, in which the hydrogen yield was assumed to be unity at a low conversion (0.06%).[3]

Results and Discussion

In the mercury-photosensitized reaction of 1,3-COD vapor, ethylene and *cis*-and *trans*-1,3,5-hexatriene were

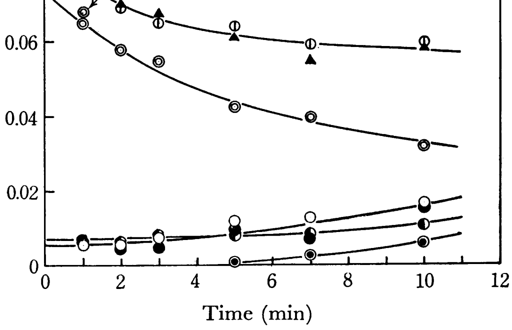


Fig. 1. Quantum yields *vs.* exposure time in the mercury-photosensitized decomposition of 1,3-COD (pressure 3 mmHg); ○, H_2; ⊙, C_2H_2; ⦶, C_2H_4; ●, benzene; ◐, 1,3-cyclohexadiene; ◎, 1,3,5-hexatriene; ▲, total C_6 (benzene+1,3-CHD+1,3,5-HT).

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[1] T. F. Thomas, C. I. Sutin, and C. Steel, *J. Amer. Chem. Soc.*, **89**, 5107 (1967).

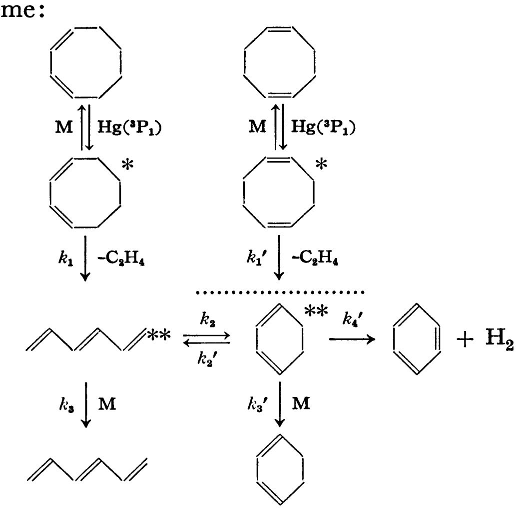
[2] S. Takamuku and H. Sakurai, *J. Phys. Chem.*, **73**, 1171 (1969); S. Takamuku, M. Utsunomiya, and H. Sakurai, *Chem. Commun.*, **1969**, 173.

[3] R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959); K. Yang, *J. Amer. Chem. Soc.*, **86**, 3941 (1964).

found to be the major initial products, together with small amounts of hydrogen, benzene, and 1,3-cyclohexadiene. Figure 1 gives the dependence of the quantum yields on the exposure time at relatively low conversions (less than 5%). The yields of these main products decreased with an increase in the irradiation time, while the minor products increased gradually. The plot also clearly shows that acetylene is newly produced by prolonged irradiation. These observations may be explained satisfactorily on the basis of the further photolysis of the main products (ethylene and 1,3,5-hexatriene), which forms hydrogen, acetylene, and 1,3-cyclohexadiene, as has been pointed out in discussing the photolyses of ethylene[4] and hexatriene[5] respectively. Thus, acetylene was not assumed to be a primary product.

The yields of the main products were unaffected by the addition of 15 mole% nitric oxide, as is shown in Figure 1, and the minor products were also essentially unaffected. These results strongly suggest an intramolecular mechanism, to the exclusion of a free radical path, for the formation of these products.

The mercury-photosensitized decomposition of 1,3-COD was studied as a function of the pressure (0.4—4.3 mmHg) in order to obtain some information on the active intermediates of this reaction. When the 1,3-COD pressure was increased, the yields of the main products increased; they showed a maximum at a pressure about 2 mmHg and then gradually decreased, probably because of the collisional deactivation of a triplet 1,3-COD molecule, while the yields of hydrogen and benzene homogeneously decreased with the pressure. Further, the pressure dependence of a path producing hydrogen and benzene seemed to be different from those of paths forming 1,3,5-hexatriene or 1,3-cyclohexadiene (the kinetic plots are shown in Fig. 2), suggesting the competing processes shown in the following scheme:



Scheme 1

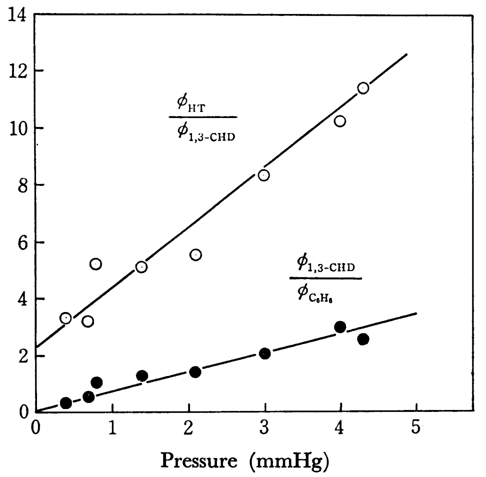


Fig 2. Kinetic plots of $\phi_{HT}/\phi_{1,3\text{-}CHD}$ and $\phi_{1,3\text{-}CHD}/\phi_{C_6H_6}$ *vs.* pressure of 1,3-COD (irradiated for 1 min); $\phi_{HT}/\phi_{1,3\text{-}CHD}$, intercept=2.4, slope=2.0 mmHg^{-1}; $\phi_{1,3\text{-}CHD}/\phi_{C_6H_6}$, slope=0.71 mmHg^{-1}.

An excited 1,3-COD molecule with a relatively long lifetime, probably a triplet state, may produce a vibrationally-excited 1,3,5-hexatriene by the simultaneous ruptures of two allylic C–C bonds in the molecule, *i. e.*, the molecular elimination of ethylene. It has been observed by Lossing[6] and by Cvetanovic[7] that, in the mercury-photosensitized decomposition of olefin, an initial rupture of the weak allylic bond occurs. The vibrationally-excited 1,3,5-hexatriene thus formed isomerizes to vibrationally-excited 1,3-cyclohexadiene, which is then subjected to collisional deactivation or dissociates to benzene and hydrogen. The pathway for the photolysis of 1,5-COD, which was proposed previously,[2,8] is also presented in the scheme (above the dotted line). It can be seen that very similar photolysis products were observed in 1,3- and in 1,5-COD.

The satisfactory material balances shown in Eqs. (1) and (2) were observed to hold under a wide variety of conditions (Fig. 1):

$$\phi_{C_2H_4} = \phi_{HT} + \phi_{1,3\text{-}CHD} + \phi_{C_6H_6} \tag{1}$$

$$\phi_{C_6H_6} = \phi_{H_2} \tag{2}$$

A steady-state treatment of the reaction scheme for 1,3-COD gives:

$$\frac{\phi_{HT}}{\phi_{1,3\text{-}CHD}} = \frac{k_3}{k_2}\left(\frac{k_4'+k_2'}{k_3'}+\mathrm{M}\right) \tag{3}$$

$$\frac{\phi_{1,3\text{-}CHD}}{\phi_{C_6H_6}} = \frac{k_3'}{k_4'}\cdot\mathrm{M} \tag{4}$$

Although there is some scatter in the data shown in Figure 2, satisfactory trends are apparent. The kinetic parameter deducible from such a treatment may permit a precise discussion of the excess energy if it is compared with that obtained from the 1,5-COD system, in which a similar reaction mechanism has been observed. In addition, such a photoelimination process of ethylene has also been found in the mercury-photosensitized decomposition of cyclooctene;[9] it seems to be characteristic of cyclic olefins.

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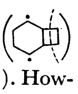
[4] R. J. Cvetanovic and A. B. Callear, *J. Chem. Phys.*, **23**, 1182 (1955).

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, **83**, 2806 (1961).

[6] F. P. Lossing, D. G. H. Marsden, and J. B. Farmer, *Can. J. Chem.*, **34**, 701 (1956).

[7] R. J. Cvetanovic and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962).

[8] In the photolysis of 1,5-COD, a biradical intermediate  was proposed for the elimination process of C_2H_4 (see Ref. 2). However, the main dissociation process was also allylic C–C bond rupture forming two 1,3-butadiene molecules.

[9] S. Takamuku, K. Moritsugu, and H. Sakurai, to be published.