Mercury Photosensitized Reaction of CycloOctatetraene

Hideo Yamazaki and Shoji Shida

FIG. 1. N. M. R. absorption derivative line for water adsorbed on TiO₂ at 0.1 monolayer (BET) at 26°C (line width, $AB=1.1$ gauss).

of 0.1 monolayer at room temperature is shown in Fig. 1. The line width from peak to peak of 1.1 gauss is to be compared with the value 16 gauss[1] for ice at $-40°C$ and 10^{-4} gauss for liquid water.

This indicates either a short relaxation time for the process of "libration" (i.e., small potential barriers) or the fact that the water molecules are sufficiently far apart so that there is little magnetic interaction between them. As the line at a coverage of approximately two monolayers has a width of 0.5 gauss the former explanation seems the most probable. Figure 2 shows the derivative line for methane adsorbed on TiO₂ at a coverage of 1.0 monolayer at 86.5°K. The width from peak to peak is 0.3 gauss.
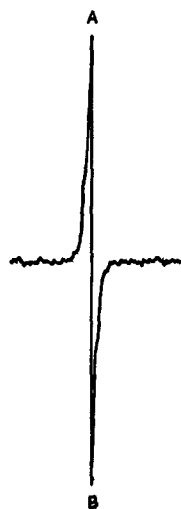

FIG. 2. N. M. R. absorption derivative line for methane adsorbed on TiO₂ at 1.0 monolayer (BET) at 86.5°K (line width, $AB=0.3$ gauss).

This result indicates that methane molecules have a relatively short relaxation time for the process of orientation on the surface both with respect to translation and rotation. This result is to be compared to the findings of Pace[2] on the thermodynamic functions of adsorbed methane at one monolayer which indicate molecular mobility on TiO₂.

The measurements were made with an apparatus similar to that already[3] described.

The TiO₂ sample was supplied by the N. J. Zinc Company, Palmerton, Pennsylvania by courtesy of T. W. Siller and consisted of C-198 acid precipitated anatase.

The residual water line shown in Fig. 1 was obtained after pumping on the TiO₂ for two days at room temperature at a pressure of 10^{-6} mm. The methane was adsorbed on this surface since the residual water line had disappeared at all temperatures at which the methane was studied.

¹ Bloembergen, Purcell, and Pound, Phys. Rev. 73, 698 (1948).
² Pace, Heric, and Dennis, J. Chem. Phys. 21, 1225 (1953).
³ Aston, Bolger, Trambarulo, and Segall, J. Chem. Phys. 22, 460 (1954).

Mercury Photosensitized Reaction of Cyclo-Octatetraene*

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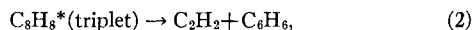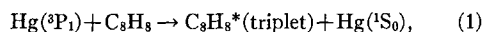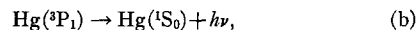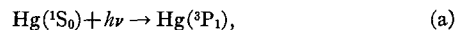(Received April 13, 1956)

THE mercury photosensitized reaction of cyclo-octatetraene has been investigated in comparison with the direct photochemical reaction using mercury resonance line, λ2537. The products of both reactions were of the same kinds, e.g., acetylene, benzene, polymer, orange-colored liquid which seems to be some isomer of cyclo-octatetraene, and a trace of styrene; the non-condensable products at liquid nitrogen temperature such as hydrogen and methane were not detected recognizably.

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 splitting off of cyclo-octatetraene.[1,2] The dependence of the rate of the decomposition on the initial pressure of cyclo-octatetraene is shown in Fig. 1.

In the case of the mercury photosensitized reaction, the rate of decomposition decreases with increasing the pressure of cyclo-octatetraene, which may be ascribed to the collisional deactivation of the excited cyclo-octatetraene molecules. The rate was reduced, however, at low pressure, owing to the incomplete quenching of the excited mercury atoms.

In the direct photochemical reaction, on the other hand, the rate of decomposition gradually increases with the increasing pressure of cyclo-octatetraene on account of the increase in total light absorbed. The pressure dependence of quantum yield for both of the above decompositions are shown in Fig. 2.

Then the following scheme may be considered for the mercury photosensitized reaction:

$$Hg(^1S_0)+h\nu \rightarrow Hg(^3P_1), \tag{a}$$

$$Hg(^3P_1) \rightarrow Hg(^1S_0)+h\nu, \tag{b}$$

$$Hg(^3P_1)+C_8H_8 \rightarrow C_8H_8^*(triplet)+Hg(^1S_0), \tag{1}$$

$$C_8H_8^*(triplet) \rightarrow C_2H_2+C_6H_6, \tag{2}$$

$$C_8H_8^*(triplet)+C_8H_8 \rightarrow 2C_8H_8 \text{ or isomer.} \tag{3}$$

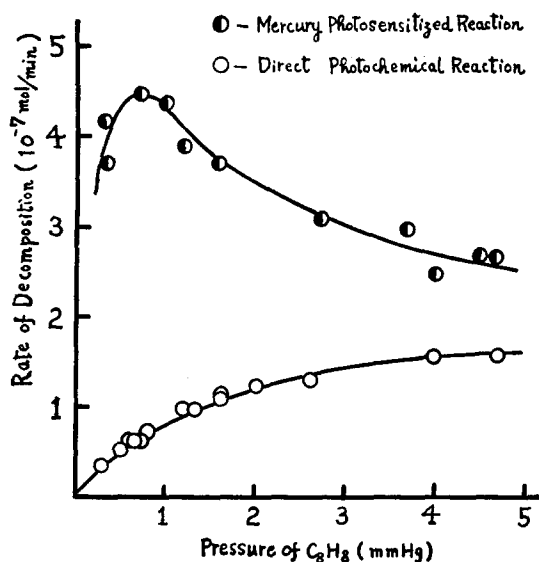Applying the steady-state treatment, the quantum yield of the

FIG. 1. Dependence of the rate of decomposition on the initial pressure of cyclo-octatetraene. The rate was measured by acetylene pressure.
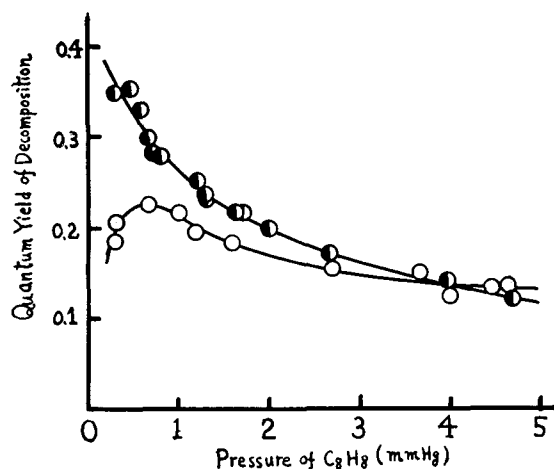
FIG. 2. Dependence of the quantum yield of decomposition on the initial pressure of cyclo-octatetraene.

decomposition is represented by the following equation:

$$\Phi = \frac{k_1 k_2 [C_8 H_8]}{(k_2 + k_3 [C_8 H_8])(k_b + k_1 [C_8 H_8])}, \qquad (I)$$

which was shown to hold satisfactorily in the pressure region studied. For the direct photochemical reaction the analogous sequence (2)–(3), including the singlet excited molecules instead of the triplet ones, is considered. The pressure corresponding to the quantum yield maximum is derived by differentiating Eq. (I), from which the quenching cross section of excited mercury atom by cyclo-octatetraene was calculated to be about 62 A,[2] taking its natural lifetime as 10^{-7} sec.[3] The value is of the same order of magnitude as those of benzene and other conjugated hydrocarbons.[4,5]

From the similarity in the kinds of products and that in the pressure dependence of quantum yield of decomposition, it may be concluded that the two reactions proceed via the same excited state (probably triplet). Cyclo-octatetraene is thus one of the rare hydrocabons which undergo efficiently the mercury photosensitized reaction as well as the direct photochemical reaction by the mercury resonance line, λ 2537.

* A part of this work was reported in J. Chem. Soc. Japan, Pure Chem. Sec. (in Japanese) 77, 500 (1956).
[1] Tanaka, Miyakawa, and Shida, Bull. Chem. Soc. Japan 24, 119 (1951).
[2] I. Tanaka and M. Okuda, J. Chem. Phys. 23, 1780 (1954).
[3] A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, p. 147 (1934).
[4] See reference 3, p. 204.
[5] Darwent, Phibbs, and Hurtubise, J. Chem. Phys. 22, 859 (1954).

Vapor Phase Crystallization of Cadmium Sulfide Crystals

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SINGLE cadmium sulfide crystals of sufficient size and quality for evaluation as scintillation counters were prepared by heating reagent grade cadmium sulfide in an oxygen-free atmosphere. The experiments were conducted in fused quartz, Vycor, and ceramic tubes at temperatures ranging from 900–1040°C for periods ranging from 16 to 48 hours. Nitrogen or argon provided the oxygen-free atmosphere. In most of the experiments, it flowed through the tubes at controlled rates and in others it was under a slight positive pressure of 3–5 pounds per square inch.

The many hundreds of experiments performed demonstrated that crystals formed nearest to the hottest portion of the tubes were always larger, sturdier, and of better quality than those
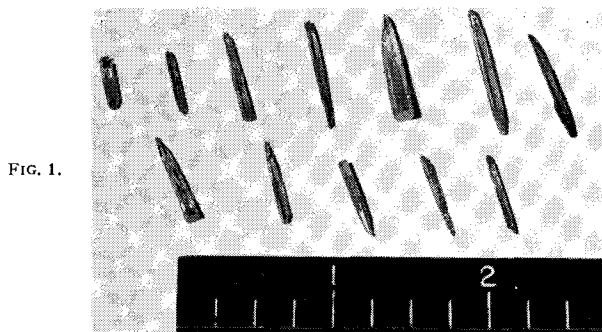

FIG. 1.

deposited toward the cooler ends. This was believed to be caused by the sharper temperature gradient in that zone of the furnace. The lowest temperature at which good quality crystals could be produced was 900°C. At this temperature and with a gas flow of 175 cc per minute, excellent ribbon-like crystals were produced in a period of 16 hours. As might be expected, the longest crystals were produced in the largest diameter tubes. X-ray diffraction patterns of the crystals demonstrated that they were the alpha type (hex.). The C-axis in the prismatic crystals was parallel to their length. In the striated plates produced in Vycor tubes, the C-axis was parallel to the surfaces. The area of the largest of these plates was about 3 sq cm. The thickness dimension of almost all the crystals of this type was slightly less than 1 mm.

TABLE I.

	Reagent	Activated	Unactivated
Ag	n.d.[a]	0.002	0.0005
Zn	0.1	0.05	0.02
Pb	0.05	n.d.	n.d.
Fe	0.05	0.005	n.d.
Mg	0.01	0.0005	0.005
Ca	0.02	n.d.	n.d.
Si	0.002	n.d.	n.d.
Cu	n.d.	n.d.	0.003

[a] n.d.—not detected.

Crystals produced in quartz tubes were of both the prismatic and plate-like type. The absence of striations in these crystals made them more suited for evaluation than those grown in Vycor tubes. Dimensions of the largest prismatic crystals grown in quartz tubes were of the order of 28 mm×3 mm×3 mm. The largest cadmium sulfide plates produced in quartz tubes were 22 mm×25 mm×1 mm. Prismatic and plate-like crystals grown in tubes of this material are shown in Figs. 1 and 2.

The step-like growth pattern of the cadmium sulfide crystals is illustrated in the photomicrograph of a portion of the edge of a plate grown in a quartz tube (Fig. 3).
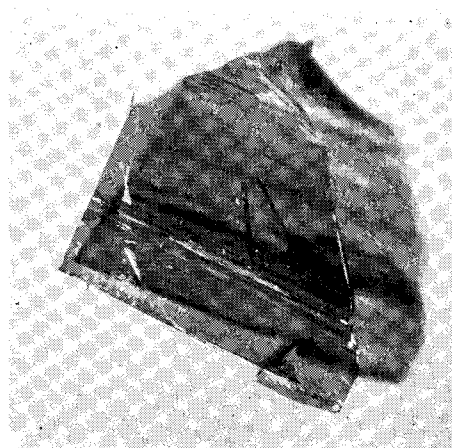

FIG. 2.