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NOTES

Hydrogen Conversion with Organic Vapor under Illumination

Anthracene and Anthracene-TNB Complex

In previous works, we have reported on the para–ortho hydrogen conversion and the hydrogen–deuterium exchange reaction in the presence of the charge-transfer complexes between polycyclic aromatic compounds and alkali metals (*1*, *2*). If we could employ these organic compounds in a *gas phase* to cause hydrogen interconversion or H_2–D_2 exchange, a unique insight would be provided into the mechanism of the catalytic activation of molecular hydrogen.

In this short note, we will present the result of a study of the hydrogen conversion in the presence of anthracene vapor and of the anthracene-trinitrobenzene (TNB) charge-transfer complex in the gas phase under illumination.

Synthesized anthracene was purified by recrystallization from a xylene solution, followed by repeated zone refining. By recrystallizations from ethanol and heptane solutions, and also by sublimation *in vacuo*, pure TNB was obtained as white plates. The complex was prepared from a carbon tetrachloride solution which contained equivalent amounts of anthracene and TNB. When the hot solution was cooled, the complex precipitated as orange, needlelike crystallites.

Figure 1 shows a schematic diagram of the experimental apparatus using a quartz reaction vessel (1) of about 50 cc volume. A 5-mg portion of each pure sample (3) was used. The samples were sublimed several times *in vacuo* in order to remove the gas included completely; then they were deposited onto the inside surface of the reaction vessel. The vessel was sealed off under a 50 mm Hg parahydrogen (or deuterium) pressure at 20°C and then heated electrically at 220°C hot enough to evaporate the compounds.

First, the measurements of the hydrogen conversion were carried out in a dark room in order to eliminate the effect of daylight irradiation on the organic vapors (this reaction is denoted as "in the dark"). To excite the organic vapor by a strong illumination, a high-pressure mercury lamp was employed (denoted as "under illumination").

The compositions of the various para–ortho hydrogen or hydrogen–deuterium mixtures before and after the reaction were measured successfully by a gas-chromatographic method. The details of the analytical method and of the preparation of parahydrogen and deuterium have already been published (*2*).

Assuming that the rate of the para–ortho hydrogen conversion obeys a first order law, the apparent rate constant, k, is as given in Table 1.

In the presence of anthracene vapor, no difference in the k value for the interconversion between the blank test and the dark conditions was found; this was also the case for the H_2–D_2 exchange reaction. Under illumination, however, a fairly strong para–ortho hydrogen conversion was observed; the rate of the conversion is given in Table 1. A slight H_2–D_2 exchange reaction occurred in this case. In the presence of the anthracene-TNB complex, only a very slow para–ortho hydrogen conversion took place in the dark, while illumination accelerated the rate of the conversion strongly.

In 1939, Farkas and Sandler reported

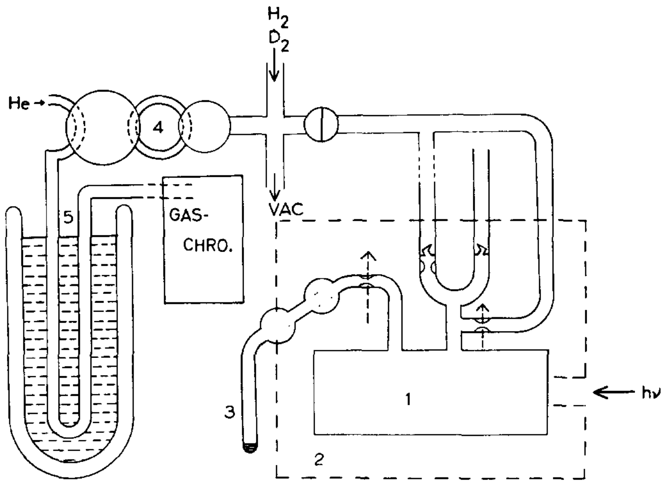

FIG. 1. The experimental apparatus of the hydrogen conversion with organic vapor: 1, quartz reaction vessel; 2, electrical furnace; 3, sample (anthracene or anthracene-TNB); 4, tap for entering hydrogen mixture to alumina column with He carrier gas; and 5, alumina column dipped in liquid nitrogen.

that a slow para–ortho hydrogen conversion takes place in a solution of liquid benzene at room temperature; they proposed that the conversion is caused by some induced magnetic moments (*3*). However, no description of the daylight effect on the conversion can be found.*

TABLE 1
THE RATE CONSTANTS OF THE PARA–ORTHO HYDROGEN CONVERSION OF ANTHRACENE AND ANTHRACENE-TNB

Compounds	k (hr^{-1}) In the dark	k (hr^{-1}) Under illumination
Blank (Glass surface)	$\sim 1 \times 10^{-3}$	$\sim 1 \times 10^{-3}$
Anthracene	$\sim 1 \times 10^{-3}$	$1.8_3 \times 10^{-2}$
Anthracene-TNB	$3.6_2 \times 10^{-3}$	$3.7_0 \times 10^{-2}$

In our study, the compounds seem to have a paramagnetic character as a result of irradiation, since the para–ortho hydrogen conversion on the vapors employed took place under illumination and since the rate of the hydrogen–deuterium exchange reaction was very slow in comparison with that of the interconversion. This paramagnetism may be considered to originate as a result of illumination, in the triplet state for the anthracene molecule, and in the excited state* for the anthracene-TNB complex.

Although the mechanism of the hydrogen and deuterium exchange reactions is not very clear at present, we believe that these simple homogeneous catalytic systems can be applied to ascertain the mechanism of the catalytic reaction.

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* In our system, anthracene vapor, we found a fairly strong acceleration of the conversion by daylight.

* The absorption spectra of the complex in the gas phase have a broad charge-transfer band around 440 mμ.