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Photochemistry in the Adsorbed Layer. III. Photolysis of Acetone Adsorbed on Porous Vycor Glass

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Photolyses of acetone adsorbed showed that the ratio of ethane to methane in the products as well as the kinetic isotope effect for the methane formation is much smaller than that in the gas phase photolysis. The methane formed from acetone-d_6 contains a considerable amount of CD_3H. Ethane formation is quenched more efficiently by nitric oxide than methane formation. It is proposed that there are two types of methyl radicals, *i.e.*, long- and short-lived ones, the ethane resulting from the long-lived radicals. The results suggest that methane arises from hydrogen abstraction from surface OH groups as well as disproportionation reaction $CH_3+CH_3CO \longrightarrow CH_4+CH_2CO$, in addition to hydrogen abstraction from acetone molecules.

Studies were carried out on the photochemistry of alkyl ketones adsorbed on porous Vycor glass, general characteristics of the photochemistry in the adsorbed layer being found.[1] In the case of 2-pentanone the photolysis was seriously affected by the surface OH groups. The studies are concerned mainly with 2-pentanone and methyl ethyl ketone and very little with acetone. In the present work a detailed study has been made of acetone photolysis. We carried out nitric oxide quenching as well as isotopic studies in order to obtain information on the nature of the methane and ethane formation processes. The role of surface OH groups in the photolysis has been clarified by the study of acetone-d_6 photolysis.

Experimental

A conventional vacuum system was used in conjunction with a special quartz cell for studying the spectra and photolysis in the adsorbed layer. The specimen of porous Vycor glass (Corning, No. 7930) which had been heated in oxygen to remove carbonaceous impurities was placed inside the cell and degassed at 500 °C for 7 hr. After acetone had been adsorbed on the specimen at room temperature, photolysis was carried out with an ultra high pressure mercury lamp without filter. Prior to this, a small amount of acetone remaining in the gas phase was removed by means of a liquid nitrogen trap. When photolysis was completed, the reaction products were desorbed together with unreacted acetone and analyzed by gas chromatography. The BET surface area of the adsorbent was found to be 160 m^2/g. The amount of adsorbed acetone of 1.0 cm^3/g corresponded to $\theta=0.05$ using 25 A^2 as the area occupied by each molecule.

Acetone (Tokyo Kasei Kogyo Co., Ltd., Grade SG. 99.5 mol%) was dried by well-degassed molecular seive 4A and purified by bulb to bulb distillation. Acetone-d_6 of 99.5 mol% isotopic purity (E. Merck, Darmstadt.) was used without further purification.

Isotopic analysis of the deuterated methane was carried out with a Shimadzu MASPEQ-070 mass spectrometer using low-voltage electron (10—20 eV) in just sufficient amount to produce the ion of the parent mass. The CD_4/CD_3H ratio was determined by measurement of the parent peaks at $m/e=19$ [CD_3H^+] and $m/e=20$ [CD_4^+].

Results

1) Products of Acetone Photolysis in the Adsorbed Layer. The rates of methane and ethane formation plotted against the amount of acetone adsorbed are given in Fig. 1. It is seen that methane formation increases with an increase in the amount of acetone adsorbed. Ethane formation appears to level off to a constant value. The ratio of the amount of methane to that of ethane ranged from 0.6 to 4.3, being larger than the corresponding value in the gas phase photolysis.[2] Our results with acetone-d_6 photolysis (25 °C, 5.05 Torr) showed this ratio to be 0.067. This suggests that the recombination of methyl radicals was suppressed and their hydrogen abstraction reaction enhanced in the adsorbed layer. A slight formation of carbon monoxide as well as greatly reduced efficiency of photolysis compared to the gas phase are other features of acetone photolysis in the adsorbed layer.

2) Isotopic Analysis of the Methane Formed. The CD_3H content of methane formed by the photolysis of acetone-d_6 adsorbed is shown in Fig. 2. A large frac-

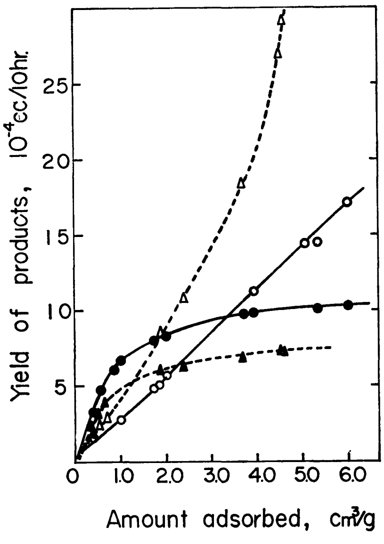

Fig. 1. Yield of products from the acetone photolysis. Irradiation time, 10 hr.; Temperature, 25 °C; △: methane, ▲: ethane (acetone), ○: methane, ●: ethane (acetone-d_6).

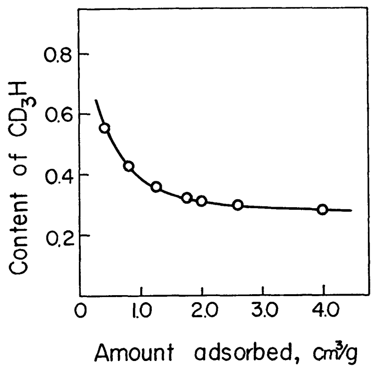

Fig. 2. The CD$_3$H content of the methane formed from the photolysis of acetone-d_6.

tion of the methane consists of CD$_3$H, decreasing with increasing amount of acetone-d_6 adsorbed. It appears that light hydrogen in the methane comes from the surface OH groups. The hydrogen atom abstraction reaction from the surface OH groups by methyl radicals, *i.e.*, $\mathrm{CD_3} + [\mathrm{Si{-}OH}] \rightarrow \mathrm{CD_3H} + [\mathrm{Si{-}O}]$, should be mentioned as the most probable process. Its activation energy is less than 9 kcal/mol,[3] being smaller than the corresponding value for the hydrogen atom abstraction from acetone molecules.[4] Thus, the hydrogen atom abstraction from the OH groups is expected to occur more easily. There is some possibility that light hydrogen atom is transferred according to the following steps:

$$\mathrm{CD_3COCD_3} + [\mathrm{Si{-}OH}] \longrightarrow$$
$$\mathrm{CD_2HCOCD_3} + [\mathrm{Si{-}OD}] \text{ (Exchange Reaction)},$$
$$\mathrm{CD_2HCOCD_3} + h\nu \longrightarrow \dot{\mathrm{C}}\mathrm{D_2H} + \mathrm{CD_3}\dot{\mathrm{C}}\mathrm{O},$$
$$\dot{\mathrm{C}}\mathrm{D_2H} + \mathrm{CD_3COCD_3} \longrightarrow \mathrm{CD_3H} + \dot{\mathrm{C}}\mathrm{D_2COCD_3}.$$

However, this could be excluded since the exchange reaction was found to be slow even under irradiation.[5] The occurrence of hydrogen atom abstraction from the surface OH groups suggests that porous Vycor glass should be regarded not only as an adsorbent but also as a photochemical reactant in the adsorbed layer.

3) Kinetic Isotope Effects for Methane Formation. In order to clarify the nature of the methane formation, the primary kinetic isotope effect for the photolysis of acetone adsorbed was investigated. The values of $\mathrm{R_{methane}}/\sqrt{\mathrm{R_{ethane}}} = \mathrm{A}$[6] are plotted against the amounts of acetone adsorbed (Fig. 3). Marked isotope effects can hardly be expected for the recombination of methyl radicals in the adsorbed layer, suggesting that the observed isotope effects are attributable to the methane formation reaction. The difference in A values is negligibly small at very small amounts adsorbed, but increases with increasing amount adsorbed, the ratio $k_\mathrm{H}/k_\mathrm{D}$ approaching 3～4. It has been reported that the ratio $k_\mathrm{H}/k_\mathrm{D}$ for the hydrogen atom abstraction reaction from acetone molecules by methyl radical in the gas phase is more than 10,[7] which is much larger than the corresponding value in the adsorbed layer. This indicates that in the photolysis of acetone adsorbed the mechanism of methane formation differs from that in the gas phase. It appears that hydrogen atom abstraction from acetone molecules is not the main reaction leading to methane formation especially in the range of small amounts of acetone adsorbed.

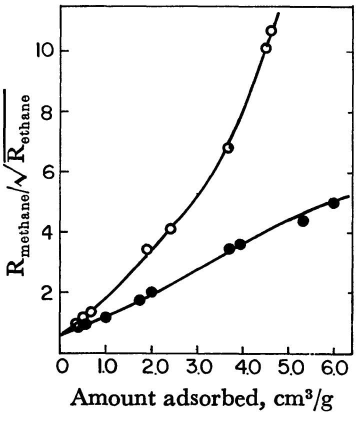

Fig. 3. The primary kinetic isotope effects for the photolysis of acetone adsorbed.
○: for acetone, ●: for acetone-d_6.

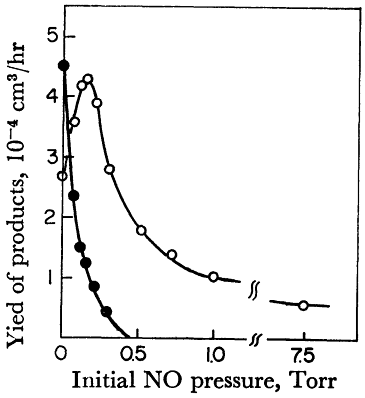

Fig. 4. Effect of nitric oxide upon the photolysis of acetone.
Amount of acetone-d_6 adsorbed, 1.91 cm³ S.T.P./g.
○: methane, ●: ethane.

4) Effect of Nitric Oxide upon Photolysis. Figure 4 shows the change in the rate of methane and ethane formation caused by added nitric oxide. The rate of ethane formation approaches zero with increasing pressure of nitric oxide, while the rate of methane formation increases at first, passes through a maximum and then decreases. Apart from a rate maximum observed in methane formation the rate decrease caused by added nitric oxide is attributable to its scavenging action of methyl radicals.[8] The pressure range in which the rate decreases is higher for methane formation than for ethane formation, suggesting that different types of

Table 1. Effect of nitric oxide upon the content of CD$_3$H

NO Pressure Torr	Content of CD$_3$H %
0.00	35.0
0.30	27.2
0.47	24.5
0.80	22.0
1.00	20.5

Amount of acetone-d_6 adsorbed, 1.91 cm³ S.T.P./g.

methyl radicals are operative in both formations. It was found that the CD_3H content in the methane formed decreased with increasing pressure of nitric oxide (Table 1).

Discussion

The following interpretation might be given as regards the two types of methyl radicals. Geminate radical pairs are held in a fixed position for a relatively long time before they separate from each other. The methyl radicals present in such radical pairs would be short-lived because of an efficient radical recombination leading to acetone formation. This primary recombination has been discussed in solution phase photochemistry. Leermakers *et al.*⁹⁾ postulated the occurrence of such phenomena in the adsorbed layer. Under such circumstances, a disproportionation reaction such as $CD_3+CD_3CO \rightarrow CD_4+CD_2CO$ would be expected to occur in addition to the recombination reaction. Such a reaction has been reported to take place to a small extent in gas²⁾ and solution phase¹⁰⁾ photolyses of acetone. The small kinetic isotope effect in methane formation (Fig. 3) suggests that methane is formed *via* a process having a small activation energy such as disproportionation of radicals. A small amount of ketene was found by mass spectroscopy in the reaction products, supporting the above conclusion. Methane formation is expected to be quenched less efficiently than reactions originated from other types of methyl radicals described below.

A methyl radical separated from its partner radical would be long-lived since it is sensitive to quenching by nitric oxide. Such methyl radicals would react in two ways, recombination to from ethane and hydrogen abstraction from acetone molecules. In cases where the abstraction reaction is the sole methane source, the rate of methane formation is expected to be larger for undeuterated acetone than for acetone-d_6 owing to its lower activation energy. As a result the rate of ethane formation will be larger for acetone-d_6. Such a behavior has been observed in the range of the amounts of acetone adsorbed above 1.0 cm^3/g (Fig. 1).

Hydrogen abstraction from the surface OH groups would be associated with both types of methyl radicals, since on addition of nitric oxide there is no marked change in the CD_3H content of the methane formed, its value decreasing from 35 to 20%.

The contribution of the three processes to the overall methane formation varies with the amount of acetone adsorbed. The contribution of hydrogen abstraction from the surface OH groups decreases with increasing amount of acetone-d_6 adsorbed (Fig. 2). Some information on the contribution of the disproportionation reaction to the overall methane formation would be obtained from the isotope effects in the formation reaction, since little or no isotope effect is expected for the disproportionation reaction as well as the hydrogen abstraction from surface OH groups in contrast with the large isotope effect for hydrogen abstraction from acetone molecules. From the marked change in isotope effects with the amount of acetone adsorbed (Fig. 3), it is concluded that below the amount adsorbed of 0.3 cm^3/g little or no hydrogen abstraction from acetone molecules takes place. Most of the CD_4 results from the disproportionation reaction, while above the amount adsorbed of 3.0 cm^3/g the predominant process in the CD_4 formation may be the hydrogen abstraction from acetone molecules.

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