Photolyses of Aliphatic Ketones Adsorbed on Porous Vycor Glass

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In contrast to extensive photochemical studies in gas phase and solution, few studies have been made on the photochemical reactions in the adsorbed layer. In the present work, photolyses of aliphatic ketones (acetone, methyl ethyl ketone and 2-pentanone) adsorbed on porous Vycor glass (Corning, No. 7930) have been investigated. After a certain amount of the vapor of ketone was allowed to be adsorbed, photolysis in the adsorbed layer was carried out at room temperature in the absence of ketone vapor. An ultra high pressure mercury lamp was used. After the photolysis, products which can be desorbed up to 100°C were analysed by gas chromatography. Prior to the experiments, the glass was oxidized in air at 600°C followed by outgassing at 500°C for 7 hr.

Photochemical reactivity of the ketones in the adsorbed layer was as follows: acetone, $R(CH_4) + R(C_2H_6)$, 0.05; methyl ethyl ketone, $R(C_2H_6)$, 1.00; 2-pentanone, $R(C_2H_4) + R(C_3H_8)$, 12.18. R(hydrocarbons) = [(Rate of formation of hydrocarbon, cc. S.T.P./hr)/(Amount of ketone adsorbed, cc. S.T.P.)] × 100. A marked difference can be seen in the reactivity of the three ketones. In contrast to the photolysis in gas phase the appearance of CO in the gas phase was negligible.[1] The results together with those in Table 1 show that in the adsorbed layer 2-pentanone undergoes the Norrish type I process ($CH_3COC_3H_7 \rightarrow CH_3CO + C_3H_7$) as well as the Norrish type II process ($CH_3COC_3H_7 \rightarrow CH_3COCH_3 + C_2H_4$). It is well-known that in gas phase and solution aliphatic ketones with γ hydrogen such as 2-pentanone undergo type II process predominantly at room temperature.[2] The results in Table 1 also show that with increasing outgassing temperature and after removal of acidic sites by nitric acid treatment,[3] $R(C_3H_8)$ decreases, while $R(C_2H_4)$ decreases little or remains unchanged. It can be concluded that the occurrence of type I process (formation of radicals) in the adsorbed layer becomes much easier on the surface with surface hydroxyl groups in a high concentration and also with acidic sites. The effect of the amount of 2-pentanone adsorbed on its photolysis was examined. As seen in Fig. 1, with the decrease of the amount adsorbed, values of $R(C_3H_8)/R(C_2H_4)$ as well as the rate of photolysis increased. Although the nature of such behavior is not clear at present, the results in Fig. 1 might be explained by assuming a heterogeneity of the glass surface.

Table 1. Photolysis of 2-pentanone adsorbed

Temp of outgassing, °C		500	800	800[a]
$R(C_3H_8)$	Type I	5.13	2.66	1.45
$R(C_2H_4)$	Type II	7.05	7.14	7.68

a) The glass was treated by nitric acid before outgassing at 800°C.

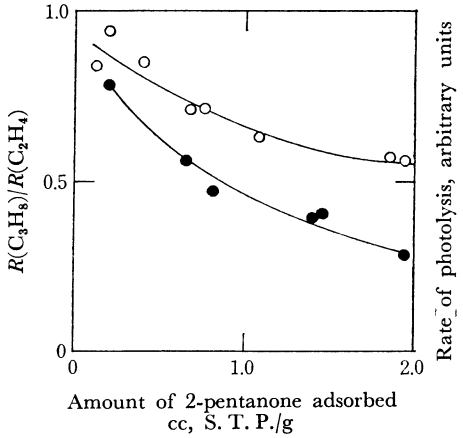

Fig. 1. Photolysis of 2-pentanone adsorbed, -○-, $R(C_3H_8)/R(C_2H_4)$; -●-, rate of photolysis.

1) In the case of 2-pentanone, both $R(CO)$ and $R(CH_4)$ were below 0.2.

2) In the gas phase photolysis of 2-pentanone, no formation of C_3H_8 occurred at 23°C and 7.3 mmHg of 2-pentanone.

3) L. H. Little, H. E. Klauser and C. H. Amberg, *Can. J. Chem.*, **39**, 42 (1961).