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Photochemistry in the Adsorbed Layer. VI. The Type I Selectivity in the Photolysis of Adsorbed 2-Pentanone

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A marked high selectivity of the type I reaction in the photolysis of adsorbed 2-pentanone decreases with increasing amount of 2-pentanone adsorbed, approaching the selectivity in the water solution photolysis. In the solution photolysis the type I selectivity decreases in the order water>methanol>*n*-heptane. From these results together with comparison of the blue shifts of the (n,π^*) bands in solution and in the adsorbed layer it has been concluded that such an enhancement of the type I reaction in the adsorbed layer is attributed to a heterogeneity of the surface, *i.e.*, the presence of special active sites, as well as to the surface polarity.

The Norrish type II reactions of alkyl ketones having γ-hydrogen atoms have been investigated by a number of workers.[1–3] On the other hand, there have been few or no studies for the type I reactions of these compounds. We have found that in the adsorbed layer the type I selectivity in the 2-pentanone photolysis is enhanced compared to that in the gas phase.[4] In order to obtain information on the nature of such enhancement, it seems necessary to investigate its photolysis in solution and to compare these results with those in the adsorbed layer. In the present work therefore it has been undertaken to study the solvent effect upon the type I selectivity in the 2-pentanone photolysis and to examine how the type I selectivity in the adsorbed layer photolysis varies with the amount adsorbed in connection with this problem.

Experimental

Materials. All the compounds used in this work were available commercially (Tokyo Kasei Kogyo Co. Ltd., Grade SG) and purified by fractional distillation. Deionized double-distilled water was degassed by alternate freezing and thawing *in vacuo*. Particular care was taken to remove water completely from the solvents and reactants. Porous Vycor glass (Corning, No. 7930) was used as adsorbent.

Apparatus and Procedure. Details of the apparatus and procedure used in the photolysis in the adsorbed layer were described in the previous paper.[4] A conventional vacuum system was used in conjunction with a special quartz cell capable of studying the spectra and photolysis in the adsorbed layer. The specimen of porous Vycor glass which had been heated in oxygen to remove carbonaceous impurities was introduced to the cell and degassed at temperatures ranging from 100 to 800 °C for 7 hr. After a certain amount of 2-pentanone had been adsorbed on the specimen, photolysis was carried out using an ultra high pressure mercury lamp without filter.

Liquid phase photolyses were carried out in a rectangular quartz cell (4.0×1.0 cm) of path length 0.5 cm, having two outlets. One was sealed off after admission and degassing of the sample solution. Another had a breakable seal which made it possible to attach the cell to a conventional analytical system after irradiation. The cell was immersed in a thermostat having a quartz window. The irradiation was carried out using an ultra high pressure mercury lamp without filter. The analytical system consisted of three traps and a modified Ward still. The gaseous products were separated by fractional distillation and analyzed by gas chromatography using a flame-ionization detector.

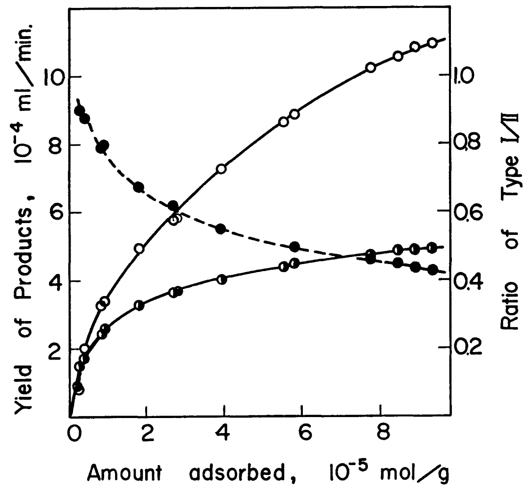

Fig. 1. Effect of amount adsorbed upon the photolysis of 2-pentanone at 25 °C. Irradiation time, 20 minutes. ○, Ethylene; ◑, Propane; ●, Ratio of Type I/II.

Results

In Fig. 1 the rates of propane and ethylene formation are plotted against the amount of 2-pentanone adsorbed. It is seen that the rates of formation increase with increasing amount adsorbed. In the range of the small amounts adsorbed the extent of the increase is large, but decreases with increasing amount adsorbed. Such a trend is more significant for the propane than for the ethylene formation. Accordingly, the ratio of propane (Norrish type I reaction) to ethylene (Norrish type II reaction) decreases with increasing amount adsorbed, finally approaching 0.40.

Results of 2-pentanone photolysis in various solvents are shown in Table 1. The major gaseous products

Table 1. The rates of 2-pentanone photolysis in various solvents[a] (10^{-4} ml/hr)

	Heptane	Methanol	Water
Ethylene	618.0	674.0	755.0
Propane	67.0	167.0	303.0
Ratio of type I/II	0.11	0.25	0.40

a) These values were the corrected rates of formation divided by the relative $\varepsilon_{\max}$ values (Table 2). The concentration of 2-pentanone was 2.0×10^{-4} mol (0.1 mol%). Photolysis was carried out at 30 °C.

formed are propane and ethylene. The amounts of minor products such as methane, ethane, propylene, and butane did not exceed 10% of the amount of propane, indicating that the rate of the type I reaction is approximately equal to the rate of propane formation. It is seen that the rate of formation increases slightly for ethylene while significantly for propane in the order heptane<methanol<water, *i.e.*, with increasing polarity of the solvents.[5-7] It should be noted that with increasing polarity of the solvent the ratio of propane to ethylene formation increases. The ratio obtained with water solution is essentially the same as the smallest corresponding value in the adsorbed layer photolysis.

TABLE 2. THE (n, π^*) TRANSITION OF 2-PENTANONE IN SOLUTION AND IN ADSORBED LAYER AT 25 °C

	Gas phase	Heptane[a)]	Methanol[a)]	Water[a)]	Vycor glass[b)]
Absorption max. (nm)	279	280	275	273	273
Relative ε_{max}	—	1.0	1.1	1.3	—

a) The concentration of 2-pentanone was 2×10^{-4} mol (0.1 mol%). b) Porous Vycor glass was pretreated at 500 °C for 7 hr in vacuum. The amount of 2-pentanone adsorbed was 9×10^{-5} mol/g. The magnitude of the blue shift of the (n, π^*) transition scarcely changed with increasing amount of 2-pentanone adsorbed.

As seen in Table 2, the blue shift of the (n, π^*) transition of 2-pentanone increases in the order *n*-heptane< methanol<water. Similar magnitudes of the blue shift have been obtained by Rao *et al.*[8] As described in the previous paper,[4] we have shown that the blue shift observed for the alkyl ketones adsorbed on porous Vycor glass is attributable to hydrogen bonding between the surface OH groups and C=O groups of the alkyl ketones and can be used as a measure of the polarity of the surface OH groups. This suggests that the surface polarity of Vycor glass may be similar to that for water solution.

Discussion

Wagner *et al.*[2,3] have carried out extensive studies of the solvent effect upon the type II reaction, which show that the rate of the type II reaction increases with increasing polarity of the solvent owing to stabilization of the 1,4-biradical intermediate, *i.e.*, a decreased probability for return of the γ-hydrogen in the biradical (formed by the intramolecular hydrogen abstraction in the excited states) due to hydrogen bonding between the polar solvent and the hydroxyl group of the biradical. The effects of the surface pretreatments upon the yields of the type II reaction of adsorbed 2-pentanone have been interpreted on a similar basis.[9] On the other hand, there have been no studies of the solvent effect upon the type I reaction. The increase in the rate of the type I reaction may be interpreted as follows: As the polarity of the solvent increases, the interaction of the radicals formed in the primary process with the solvent will increase. Such an increase in the interaction would result in the increase in stabilization of the radicals, leading to suppression of the recombination of the alkyl-acyl radical pairs formed in the primary process as well as increased probability of α-cleavage in the excited triplet states, *i.e.*, formation of these radical pairs. Both effects may contribute to enhancement of the yield of the type I reaction.

In the range of the amount adsorbed about 9.00×10^{-5} mol/g the magnitude of the blue shift of the (n, π^*) transition as well as the ratio of the yield for the type I to that for the type II reaction is essentially the same as that observed for water solution. This suggests that at least in this range of the amount adsorbed enhancement of the type I reaction in the adsorbed layer may arise from the surface polarity which is reflected by the magnitude of the blue shift. Such a significant role of the surface polarity in determining the ratio of the yield for the type I to that for the type II reaction is apparent from the effect of surface pretreatments upon the photolysis of adsorbed 2-pentanone described previously.[9] As seen in Fig. 2 this ratio decreases with increasing degassing temperature, *i.e.*, with decreasing surface polarity owing to the decrease in the concentration of surface OH groups.

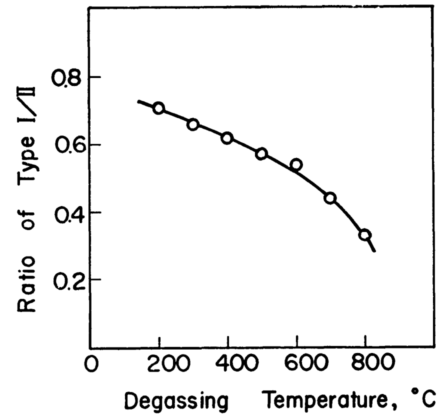

Fig. 2. Effect of degassing temperature upon the photolysis of adsorbed 2-pentanone at 25 °C. Amount of 2-pentanone adsorbed was 2.2×10^{-5} mol/g.

In the range of the amount adsorbed below 4.00×10^{-5} mol/g a marked increase in the type I selectivity as well as the overall yield of the photolysis occurs. Although the true nature of such a marked increase in the type I selectivity is not yet clear, such behavior may be explained by assuming a heterogeneity of the surface, *i.e.*, the presence of special active sites, since the amount adsorbed of 4.5×10^{-5} mol/g corresponds to $\theta=0.05$ using 25 A^2 per one molecule.

It has been reported by Turkevich and Fujita,[10] and by Gesser and his co-workers[11,12] that the radicals produced by the photolysis of methyl iodide adsorbed on porous Vycor glass are trapped much more strongly on a limited number of active sites than other sites. Thus, a significant increase in the radical stabilization would be expected on such special active sites, where suppression of the recombination of the radical pair as well as an increase in the probability of α-cleavage described above would be much more significant than that for other ordinary sites. In addition, it seems necessary to take into account the following possibility: The type I reaction will be enhanced because of the contribution of hydrogen abstraction from the surface OH groups, which takes place more efficiently in the small amounts adsorbed as described in the previous paper.13) Furthermore, the presence of special active sites capable of abstracting hydrogen efficiently from 2-pentanone molecules may retard the intramolecular γ-hydrogen abstraction leading to the type II reaction. The presence of such kind of active sites has already been suggested by Low *et al.*14) for the Vycor glass–acetone system.

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