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Photochemistry in the Adsorbed Layer. V. Effects of Surface Pretreatments upon the Photolysis of Adsorbed 2-Pentanone

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The effects of surface pretreatment upon the photolysis as well as the absorption and phosphorescence spectra of 2-pentanone adsorbed on porous Vycor glass have been investigated. The rate of propane formation (Norrish type I reaction) passes through a maximum and then decreases at higher degassing temperatures, while that of ethylene formation (Norrish type II reaction) decreases with increasing degassing temperature. Simultaneously, the phosphorescence intensity increases while the blue shift of the (n,π^*) band decreases. This suggests that with a rise in degassing temperature the triplet lifetime increases while the surface polarity decreases. Thus, the decrease in the rate of ethylene formation is attributed to destabilization of the 1,4-biradicals formed by the intramolecular hydrogen abstraction, and the decrease in the rate of propane formation to the decrease in the lifetime of the *n*-propyl radicals, the hydrogen abstraction efficiency, and the probability of α-cleavage.

Photolysis as well as absorption and phosphorescence spectra of acetone, methyl ethyl ketone, and 2-pentanone adsorbed on porous Vycor glass have been investigated recently.[1)] It was shown that acetone most strongly hydrogen bonded to the surface OH groups exhibits the most efficient radiationless deactivation. It was found that in the photolysis of adsorbed 2-pentanone Norrish type I reaction occurs to a larger extent than that in the gas phase photolysis.[2)]

It is well-known that the concentration of surface OH groups and their reactivity markedly change after surface pretreatment such as heat[3)] or fluoridation pretreatment.[4)] It is expected therefore that the interaction of alkyl ketones with the surface OH groups would be seriously affected by such surface treatment. We have investigated the effects of surface pretreatment upon the photochemistry of adsorbed 2-pentanone in order to obtain information on the nature and reactivity of the excited states.

Experimental

Details of the apparatus, procedures, and materials were described previously.[1)] A conventional vacuum system was used in conjunction with a special quartz cell capable of studying the spectra and photolyses in the adsorbed layer. The specimen of porous Vycor glass which had been heated in oxygen to remove carbonaceous impurities was introduced into the cell and degassed at temperatures 100—800 °C for 7 hr. After 2-pentanone had been adsorbed on the specimen, photolysis was carried out using an ultra high pressure mercury lamp without filter. The amount of 2-pentanone adsorbed was 2.19×10^{-5} mol/g. The BET surface area[5)] of the specimen remained unchanged until 500 °C, decreasing at higher temperatures from 160 m^2/g at 500 °C to 140 m^2/g at 700 °C. In the case of NH_4F pretreatment, the specimen was dried at 100 °C and then degassed at 800 °C for 7 hr. After such treatment the BET surface area was reduced to about 60% of its initial value. The IR spectra after the treatment indicate that about 60—65% of the surface OH groups was removed.

Results

Effects of Degassing Temperature upon Absorption and Phosphorescence Spectra. Figure 1 shows the blue shifts of the (n, π^*) transition of adsorbed 2-pentanone and methyl ethyl ketone against the degassing temperature. It is seen that the magnitude of the blue shift decreases with a rise in degassing temperature. It is well-known that the (n, π^*) transition of the ketones is blue shifted in polar solvents due to hydrogen bonding, its magnitude increasing with the polarity of the solvent.[6)] Since alkyl ketones are adsorbed on porous Vycor glass by hydrogen bonding between the surface OH groups and C=O groups of the ketone, such a decrease in the blue shift with increasing degassing temperature is attributable to a decrease in the polarity of the surface OH groups. The change in the number of surface OH groups/g with degassing temperature obtained by Low and Ramasubramanian[3)] is given in Fig. 2. A similar relative change in the number of OH groups with the degassing temperature was obtained with our specimen from the intensity measurements of the band at 3750 cm^{-1}. This suggests that the surface polarity decreases with decreasing

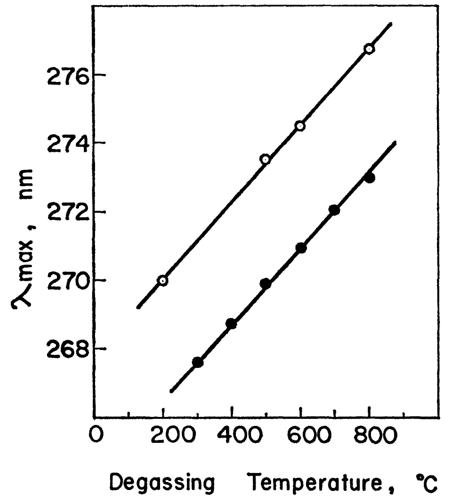


Fig. 1. Effect of degassing temperature upon the (n, π^*) transition of the ketones adsorbed. The amounts of adsorbed methyl ethyl ketone and 2-pentanone were 2.37×10^{-5} mol/g and 2.10×10^{-5} mol/g, respectively. ●, methyl ethyl ketone; ○, 2-pentanone.

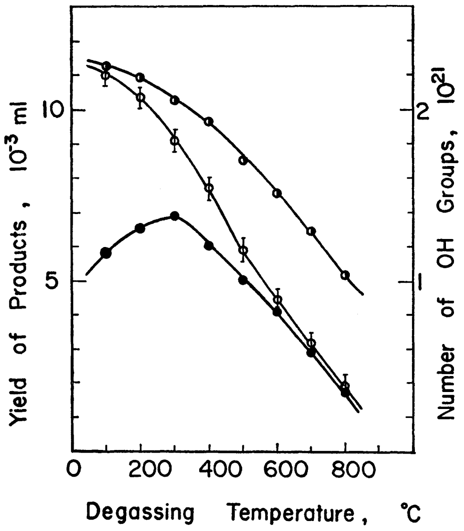


Fig. 2. Effect of degassing temperature upon the yield of products from the 2-pentanone photolysis. Amounts of adsorbed 2-pentanone was 2.19×10^{-5} mol/g. Irradiation time, 20 minutes; Temperature, 25 °C. Φ, the number of OH groups/g; ◑, ethylene; ●, propane.

TABLE 1. EFFECT OF DEGASSING TEMPERATURE UPON THE PHOSPHORESCENCE INTENSITY OF 2-PENTANONE ADSORBED

Temperature °C	Amount adsorbed 10^{-5} mol/g	Phosphoresence max. nm	Relative intensity
300	7.01	445±5	1.00
500	7.01	450±5	1.23
700	7.01	455±5	1.70
300	20.1	445±5	1.00
700	20.1	455±5	1.68

concentration of the surface OH groups.

A similar behavior has been reported by Glass and Ross[7] who found that the heat of adsorption of hydrogen sulfide adsorbed on silica gels by hydrogen bonding decreased with increasing degassing temperature, *i.e.*, with decreasing concentration of the surface OH groups.

Table 1 shows the effect of the degassing temperature upon the phosphorescence spectra of adsorbed 2-pentanone, its intensity increasing with increasing degassing temperature. Taking into account the fact that there was no change in the relative intensity of the absorption spectra with a rise in degassing temperature, such a decrease in the phosphorescence intensity is attributable to a decrease in the population of the excited triplet ketone molecules.[8] The more blue shifted, *i.e.*, the more strongly hydrogen bonded a ketone molecule is, the more efficient radiationless deactivation becomes.[1] Thus, the decrease in the concentration of the triplet molecules is attributable to the increase in the radiationless deactivation efficiency.

Effect of Surface Pretreatment upon Type I and II Reactions. The major gaseous products in the photolysis of adsorbed 2-pentanone are ethylene (type II) and propane (type I).[1] The effect of degassing temperature upon the rates of type I and II reactions is shown in Fig. 2. With increasing degassing temperature the rate of type II reaction decreases while the rate of type I reaction passes through a maximum and then decreases at higher degassing temperatures.

TABLE 2. EFFECT OF SURFACE PRETREATMENTS UPON THE PHOTOLYSIS OF 2-PENTANONE ADSORBED

Condition of pretreatment[a]	Yield of propane 10^{-2} ml/hr	Yield of ethylene 10^{-2} ml/hr	Value of propane/ethylene
No-treatment	0.88	2.00	0.44
NH_4F solution	2.09	2.01	1.04

a) The specimens were degassed at 800 °C. Amount of 2-pentanone adsorbed was 1.43—1.70 mol/g. Minor products; CO, CH_4, C_2H_6, C_6H_{12}. CH_3COCH_3 was not determined.

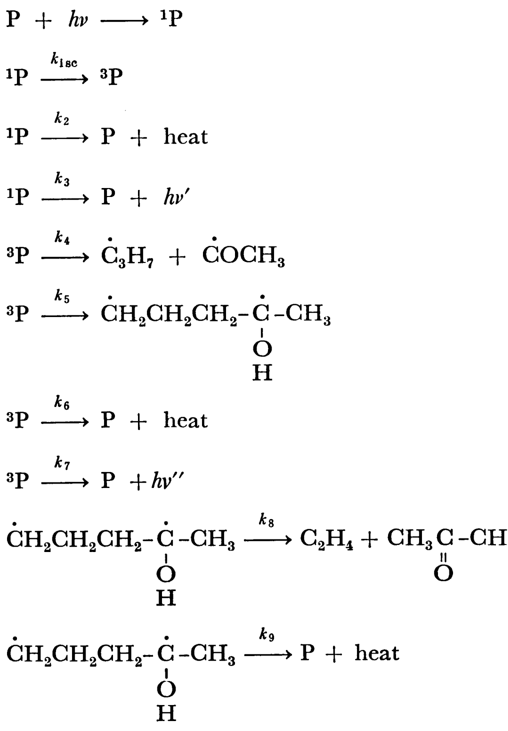
The results of the NH_4F treatment are given in Table 2. Taking into account a decrease in the surface area after the treatment, it is concluded that both type II and type I reactions are enhanced after the treatment, its extent being larger for the latter than for the former. According to the work of Chapman and Hair,[4] after NH_4F pretreatment the surface consists of silanol groups (Si–OH) and F atom attached to Si atoms on the surface. Owing to the electronegativity of F atoms, the weakening of the O–H bond takes place, resulting in the increase in surface acidity or surface polarity. Thus, essentially the same trend was observed for both experiments, suggesting a significant role of the polarity of the surface OH groups in determining the rates of product formation.

Discussion

Type II Reaction. Type II reactions of alkyl ketones having γ-hydrogen atoms have been investigated by many workers.[9–12] According to Yang and Elliot[9] who investigated the type II reaction of the optically active ketone, 5-methyl-2-heptanone, there seems to be no doubt that the reaction proceeds *via* 1,4-biradicals formed by the intramolecular hydrogen abstraction.

Wagner found that the type II reaction is enhanced in polar solvents in comparison with in nonpolar solvents.[10] The quantum yield of the residual singlet reaction, however, which remains after addition of sufficient amounts of diene to quench all the excited triplet ketone molecules, is the same in all solvents.[10,13] This suggests that polar solvents should increase the efficiency of type II reactions from the alkyl ketone excited triplet state. This effect has been attributed by Wagner to a decreased probability for return of the γ-hydrogen in the 1,4-biradical, formed by the intramolecular hydrogen abstraction in the excited triplet states, due to hydrogen bonding between the polar solvent and the hydroxyl group of the biradical.

The ethylene formation from adsorbed 2-pentanone decreases with increasing degassing temperature. The surface polarity or acidity decreases with increasing degassing temperature. The following tentative conclusion may be drawn: In the photolysis of adsorbed 2-pentanone only the ethylene formation from the triplet excited states would be affected by the change in the degassing temperature. The decrease in ethylene formation with increasing degassing temperature is associated with the decrease in surface polarity which results in destabilization of the 1,4-biradicals. The photolysis of the absorbed 2-pentanone may be represented by the following scheme:



$$P + h\nu \longrightarrow {}^1P \qquad (1)$$

$${}^1P \xrightarrow{k_{isc}} {}^3P \qquad (isc)$$

$${}^1P \xrightarrow{k_2} P + \text{heat} \qquad (2)$$

$${}^1P \xrightarrow{k_3} P + h\nu' \qquad (3)$$

$${}^3P \xrightarrow{k_4} \dot{C}_3H_7 + \dot{C}OCH_3 \qquad (4)$$

$${}^3P \xrightarrow{k_5} \dot{C}H_2CH_2CH_2\text{-}\overset{\bullet}{\underset{\substack{|\\ O\\ H}}{C}}\text{-}CH_3 \qquad (5)$$

$${}^3P \xrightarrow{k_6} P + \text{heat} \qquad (6)$$

$${}^3P \xrightarrow{k_7} P + h\nu'' \qquad (7)$$

$$\dot{C}H_2CH_2CH_2\text{-}\overset{\bullet}{\underset{\substack{|\\ O\\ H}}{C}}\text{-}CH_3 \xrightarrow{k_8} C_2H_4 + CH_3\underset{\substack{\|\\ O}}{C}\text{-}CH_3 \qquad (8)$$

$$\dot{C}H_2CH_2CH_2\text{-}\overset{\bullet}{\underset{\substack{|\\ O\\ H}}{C}}\text{-}CH_3 \xrightarrow{k_9} P + \text{heat} \qquad (9)$$

(Reaction Scheme 1)

Reaction 9 is the radiationless deactivation process which proceeds *via* a return of γ-hydrogen in the 1,4-biradical. Using the steady state approximation in the excited states, the rate of type II reaction can be represented by

$$\text{Rate}_{(C_2H_4)} = \left(\frac{k_5}{k_4+k_5+k_6+k_7}\right)\left(\frac{k_8}{k_8+k_9}\right)I_p\Phi_{isc} \qquad (I)$$

where I_p is the rate of light absorption by molecule P and Φ_{isc} the efficiency of the intersystem crossing.

With increasing degassing temperature the 1,4-biradical lifetime τ_b, *i.e.*, $(k_8+k_9)^{-1}$ decreases owing to an increase in k_9. The phosphorescence measurements suggest that the triplet lifetime τ_t, *i.e.*, $(k_4+k_5+k_6+k_7)^{-1}$ increases with increasing degassing temperature. The magnitude of the decrease in the biradical lifetime would be larger than that of the increase in the triplet lifetime, since the rate of ethylene formation decreases with increasing degassing temperature.

Type I Reaction. The rate of propane formation can be represented as follows: In addition to scheme 1 the following reactions are included;

$$\dot{C}_3H_7 + [H] \xrightarrow{k_{10}} C_3H_8 \qquad (10)$$

$$[\dot{C}_3H_7 + \dot{C}OCH_3]_{ads} \xrightarrow{k_{11}} \text{Recombination or Disproportionation Products} \qquad (11)$$

$$R_{(C_3H_8)} = k_{10}[H][\dot{C}_3H_7] = \left(\frac{k_4}{k_4+k_5+k_6+k_7}\right)\left(\frac{k_{10}[H]}{k_{10}[H]+k_{11}[\dot{C}OCH_3]}\right)I_p\Phi_{isc} \qquad (II)$$

The rate of propane formation is determined by hydrogen abstraction efficiency, $k_{10}[H]$, as well as the steady state concentration of the propyl radicals. In the photolysis of acetone-d_6 adsorbed on porous Vycor glass the methane formed contained 55% of CD_3H at the amount adsorbed of 2×10^{-5} mol/g.[14] This suggests that in the case of the photolysis of adsorbed 2-pentanone the hydrogen abstraction from the surface OH groups would contribute considerably to the overall propane formation at least in the range of the small amounts adsorbed. Accordingly, the hydrogen abstraction efficiency $k_{10}[H]$ would decrease with increasing degassing temperature owing to the decrease in the concentration of the surface OH groups.

The steady state concentration of the propyl radicals is determined by the propyl radical and triplet 2-pentanone lifetime as well as by the k_4 value (Eq. (II)). The change in the radical lifetime with degassing temperature can be determined by the effect of oxygen pressure upon the propane formation,[15] by means of the Stern-Volmer relationship

$$\frac{Q_0}{Q} = 1 + \tau_r k_s[O_2]$$

where τ_r is the radical lifetime and k_s the scavenging rate constant with oxygen. Q and Q_0 are the rates of propane formation in the presence and absence, respectively, of oxygen. Assuming that the value of k_s scarcely changes with degassing temperature, the change in the radical lifetime with degassing temperature is obtained from the Stern-Volmer plots. The lifetime of propyl radicals decreases with increasing degassing temperature (Fig. 3). Remem-

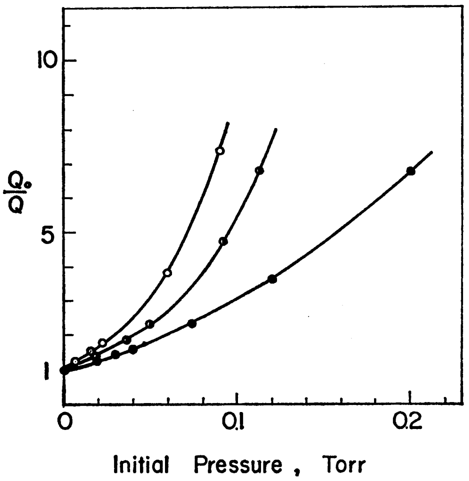


Fig. 3. Stern-Volmer plot for scavenging of the propane formation with oxygen. ○, pretreated at 300 °C; ◑, pretreated at 500 °C; ●, pretreated at 700 °C.

bering that the hydrogen abstraction efficiency $k_{10}[H]$ decreases with increasing degassing temperature, it is concluded that the increase of $(k_{10}[H]+k_{11}[\dot{C}OCH_3])$ and the decrease of $k_{10}[H]$ occurs simultaneously. This suggests that the contribution of $k_{10}[H]$ to the value of $(k_{10}[H]+k_{11}[\dot{C}OCH_3])$ is rather small. In other words, the lifetime of the propyl radicals is determined mainly by the value of $k_{11}[\dot{C}OCH_3]$, which refers to the reaction of *n*-propyl–acetyl radical pairs such as the recombination and disproportionation reactions.[16] Such an increase in the value of $k_{11}[\dot{C}OCH_3]$ with increasing degassing temperature would be expected since the magnitude of k_{11} depends upon the surface mobility of the radicals, which will increase with decreasing strength of the interaction between the radicals and the surface OH groups. The weak interaction of the radicals with the Vycor glass surface pretreated at a higher temperature was also studied by Garbutt and Gesser by means of ESR technique.[17]

Such a decrease in the strength of the interaction between the radicals and the surface with increasing degassing temperature suggests the decrease in stabilization of the radicals formed in the primary process, which would be expected to result in a decreased probability of α-cleavage, *i.e.*, a decreased k_4 value. It is concluded that the decrease in the propane formation with increasing degassing temperature is attributable to a decreased probability of α-cleavage as well as the decrease in the radical lifetime and the hydrogen abstraction efficiency. In the temperature range where no decrease in these values occurs it is expected that the propane formation increases with increasing degassing temperature owing to the increase in the lifetime of the triplet excited ketone molecules. It appears that such a situation is realized in the temperature range below 300 °C. Thus, a maximum in the propane formation is explicable.

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15) In general, the decrease in propane formation by oxygen arises from the quenching of the triplet excited states as well as of the radicals. The Stern-Volmer plots were found to be non-linear (Fig. 3). It was confirmed,[1] however, that in the pressure range below 10^{-1} Torr the radical scavenging is the predominant process.

16) Reaction of $\dot{C}_3H_7+\dot{C}OCH_3\rightarrow C_3H_7COCH_3$ and reaction of $\dot{C}_3H_7+\dot{C}OCH_3\rightarrow C_3H_8+CH_2CO$ (or $\dot{C}_3H_7+\dot{C}OCH_3\rightarrow C_3H_6+CH_3COH$) take place. Some evidence supporting the disproportionation reaction has been given.[14]

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