BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (9), 2623—2624 (1976)

Photochemistry in the Adsorbed Layer. VII. Steric Hindrance in the Type II Cleavage of Adsorbed Alkyl Ketones

Masakazu Anpo and Yutaka Kubokawa
Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591

(Received March 16, 1976)

Synopsis. The type I selectivity in the photolysis of adsorbed alkyl ketones is larger for 3-methyl-2-pentanone than for 2-pentanone. Such behavior can be explained by the concept that the type II cleavage is more hindered for the former owing to a steric hindrance arising from the presence of a solid surface.

Recently we have investigated the spectra and photochemistry of alkyl ketones adsorbed on porous Vycor glass and found the general characteristics of the photochemistry in the adsorbed layer.[1–6] The change in the photochemical reactivity caused by adsorption has been discussed mainly from the electronic aspects. It seems likely that such a change in the photochemical reactivity is attributed in part to the steric effect arising from the presence of a solid surface. An example of this steric effect has been found in the type II cleavage of adsorbed alkyl ketones. The results are described in the present paper.

Experimental

Materials. 3-Methyl-2-pentanone (Tokyo Kasei Kogyo Co., Ltd.) was purified by preparatory chromatography and then vacuum distilled bulb-to-bulb. Analysis by vapor phase chromatography equipped with flame ionization detection showed no impurity. Porous Vycor glass (Corning, No. 7930) was used as an adsorbent.

Apparatus and Procedure. Details of the apparatus and procedures were described previously.[1–6] A conventional vacuum system was used in conjuction 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 into the cell and degassed at 500 °C for 7 h. Photolysis was carried out using an ultra high pressure mercury lamp without filter, after ketone molecule had been adsorbed on the specimen. Analysis was carried out by vapor phase chromatography using a 3 m column of porapak Q for hydrocarbons and a 2 m column of molecular sieve 5A for the noncondensable gases.

Results and Discussion

The results of the photolysis of adsorbed 3-methyl-2-pentanone (3-M-2-P) at room temperature are given in Table 1, and those of its photolysis in the gas phase in Table 2. In the gas phase photolysis the rate of ethylene formation is three times higher than that of radical product formation. Such behavior is in agreement with that reported by other workers,[7] who showed that the type II reaction is predominant in the gas phase (below 30 °C) and in solution. Comparison of Tables 1 and 2 show that the rate of radical product formation in the adsorbed layer is much higher than that of ethylene formation. Results of the photolysis of adsorbed 2-pentanone (2-P)[1,6] are given in Table 1. It is seen that the type I selectivity is higher in the adsorbed layer than in the gas phase, its extent being much larger for 3-M-2-P than for 2-P. Furthermore, the marked increase observed in going from 2-P to 3-M-2-P arises mainly from the decrease in the rate of ethylene formation. Such a high type I selectivity in the adsorbed layer was attributed to suppression of the recombination of the radical pairs as well as increased probability of α-cleavage, leading to the increase in the rate of radical product formation.[6] However, it is difficult to explain the marked higher type I selectivity of 3-M-2-P as compared to that of 2-P.

Table 1. Results of the photolysis of adsorbed alkyl ketones at 25 °C[a]

	Amount adsorbed[b] 10^{-6} mol/g	Yield of type II 10^{-3} ml/5 min	Yield of[c] type I 10^{-3} ml/5 min	Selectivity (type I/II)
3-Methyl-2-pentanone	5.36	0.21	1.07	5.1
	21.40	0.48	2.21	4.6
	42.80	0.65	2.59	4.0
2-Pentanone[d]	4.28	0.72	0.65	0.89
	22.00	1.92	1.24	0.65

a) The molar extinction coefficient at the wavelength of maximum absorption, ε for 3-methyl-2-pentanone was 1.45 times larger than that for 2-pentanone in the adsorbed layer. This ratio hardly changed with increasing amount of the ketone adsorbed.[2] b) The amount adsorbed of 4.47×10^{-6} mol/g corresponds to $\theta=0.005$ using 25 A^2 as the area that occupied by each molecule. As the amount adsorbed decreases, a marked increase in the type I selectivity as well as in the overall efficiency of the photolysis occurs (Table 2). Such a behavior would be attributed to a heterogeneity of the surface, *i.e.*, the presence of special active sites.[6] c) The amounts of minor products such as methane, propane, butene, and hexane did not exceed 15% of the amount of butane, indicating that the rate of the type I reaction is approximately equal to the rate of butane formation. d) M. Anpo and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **48**, 3085 (1975).

In order to obtain information on the nature of the excited states in the photolysis, the effect of added nitrogen oxide on ethylene formation from adsorbed 3-M-2-P has been investigated in a similar manner to that described previously.[1] The maximum reduction of ethylene formation by added nitrogen oxide, *i.e.*, the formation of ethylene from the triplet excited state, was about 47%, almost the same as the corresponding value observed

Table 2. Results of the photolysis of gaseous 3-methyl-2-pentanone at 30 °C

Relative	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8	C_5H_{12}	C_6H_{14}
Yield	1.45	1.90	100.0	0.65	4.30	16.6	1.56	5.70	8.20

3-Methyl-2-pentanone pressure, 18.0±0.5 Torr. Irradiation time, 15 min. Selectivity was identified as $(\phi_{C_3}+\phi_{C_4}+\phi_{C_5}+\phi_{C_6})/(\phi_{C_2H_4})$.

with 2-P. There was no marked difference in the lifetimes of the triplet states of 2-P and 3-M-2-P determined from the Stern-Volmer plots for ethylene quenching with nitrogen oxide. This suggests that there is no difference in the nature on the excited states in the adsorbed layer photolysis between both ketones.

The type II reaction proceeds *via* 1,4-biradical intermediate formed by the intramolecular hydrogen abstraction.[8] A favorable conformation would be necessary for such γ-hydrogen abstraction to take place. A six-membered transition state has been proposed for this reaction. On a solid surface the rapid tumbling motion of molecules would be hindered, formation of such a six-membered transition state being disturbed. The steric hindrance would be expected to be more significant for 3-M-2-P than for 2-P owing to the presence of a bulky methyl group instead of a hydrogen. Thus, the marked lower rate of ethylene formation observed with the former as compared to the latter is explicable. Such steric requirements for the type II cleavage have been proposed by Turro and Weiss[9] who found a marked difference in the photochemical behavior of *cis* and *trans*-2-propyl-4-*t*-butylcyclohexanones in cyclohexane solution.

References

1) Y. Kubokawa and M. Anpo, *J. Phys. Chem.*, **78**, 2442 (1974).

2) M. Anpo and Y. Kubokawa, *J. Phys. Chem.*, **78**, 2446 (1974).

3) M. Anpo, S. Hirohashi, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **48**, 985 (1975).

4) Y. Kubokawa and M. Anpo, *J. Phys. Chem.*, **79**, 2225 (1975).

5) M. Anpo, T. Wada, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **48**, 2663 (1975).

6) M. Anpo and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, **48**, 3085 (1975).

7) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4009 (1965); F. S. Wettack and W. A. Noyes, Jr., *ibid.*, **90**, 3901 (1968).

8) N. C. Yang, S. P. Elliott, and B. Kim, *J. Am. Chem. Soc.*, **91**, 7551 (1969); N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972), and references therein.

9) N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90**, 2185 (1968).