

The Effect of Surface Hydroxyl Groups upon the Deactivation of Excited  
Triplet Acetone Adsorbed on Porous Vycor Glass

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H-D exchange between deuterated surface hydroxyl groups and excited triplet acetone has been observed on porous Vycor glass, proceeding via a surface hydroxyl group-assisted photoenolization of acetone. This chemical process evidences that surface hydroxyl groups play a significant role in determining the fate of the excited triplet acetone adsorbed on Vycor glass by a strong hydrogen bonding.

Photochemistry of molecules adsorbed on inert adsorbents such as  $\text{SiO}_2$  has attracted a great deal of attention from the standpoint of photochemical processes on solid surfaces in connection with photochemical-vapor-deposition, as well as the potential possibility of controlling the photochemical reaction in yield and selectivity.<sup>1-6)</sup> In the previous series, the author has investigated the photochemistry of alkyl ketones adsorbed on porous Vycor glass and found that their photochemical reactivities are markedly different from those in the gaseous phase, leading to some general characteristics of the photochemistry in the adsorbed states.<sup>1,7)</sup>

Although effects of surface hydroxyl groups upon the secondary processes in the photochemical reaction of adsorbed alkyl ketones have been clarified,<sup>1,7)</sup> their roles in the primary processes have been scarcely investigated. To investigate this problem, the photo-induced H-D exchange reaction between acetone- $d_6$  (or acetone) and surface OH groups (or surface OD groups) on porous Vycor glass is dealt in the present work.

Transparent porous Vycor glass (PVG) (Corning code; 7930, major composition;  $\text{SiO}_2 \cong 96\%$  and  $\text{B}_2\text{O}_3 \cong 3\%$ , BET surface area;  $150\text{-}160 \text{ m}^2/\text{g}$ ) was used as an

adsorbent. Acetone- $d_6$  of 99.5 mol% isotopic purity (E. Merck Darmstadt) was used without further purification. Acetone was allowed to be adsorbed at 295 K on the glass specimen which had been degassed at 773 K for 7 h (standard pretreatment). The amount of adsorbed acetone was about  $(4.5 - 220) \times 10^{-6}$  mol/g, which corresponds to the coverage  $\theta = 0.0018 - 0.072$  for surface OH groups as adsorption sites. In the case of deuteration of surface OH groups, the glass specimen was treated with  $D_2O$  at 423 K and then degassed at 673 K, and this process was repeated several times. UV irradiation was carried out with a high pressure mercury lamp (Toshiba SHL-100UV) with a color filter and a water filter ( $\lambda > 280$  nm). Isotopic analysis of the deuterated acetone was carried out with a Shimadzu MASPEQ-070 mass spectrometer. IR spectra of surface OH groups were measured with a Hitachi IR-G<sub>2</sub> and a Shimadzu IR-460. Phosphorescence spectra were measured at 77 K with a Shimadzu RF-501 spectrofluorophotometer with a color filter to eliminate scattered light. Phosphorescence decay curves were obtained by using an N<sub>2</sub>-laser excitation system with 5 ns pulse width. Experimental details have been described elsewhere.<sup>1,7)</sup>

After adsorption on PVG, acetone exhibits a large blue shift in the  $(n, \pi^*)$  absorption band due to the hydrogen bonding between =C=O group and surface OH group.<sup>1,7)</sup> Figure 1 shows the photoluminescence spectrum of acetone molecules adsorbed on PVG and the effect of added NO molecules upon the emission. By the addition of NO or O<sub>2</sub> molecules as a triplet quencher, the emission was easily quenched. From these results, together with a good accordance of the emission with the phosphorescence of acetone measured at 77 K in EPA matrix,<sup>8)</sup> except for a blue shift of ca. 10 nm, the observed photo-emission was assigned to the phosphorescence of acetone adsorbed on PVG. The decay curve of phosphorescence was found to be bi-exponential with lifetimes of  $\tau_1 = 6.7$  and  $\tau_2 = 1.1$   $\mu$ s. These components are tentatively attributable to the excited triplets of acetone adsorbed on  $\text{>Si-OH}$  and  $\text{>B-OH}$  groups, respectively, since

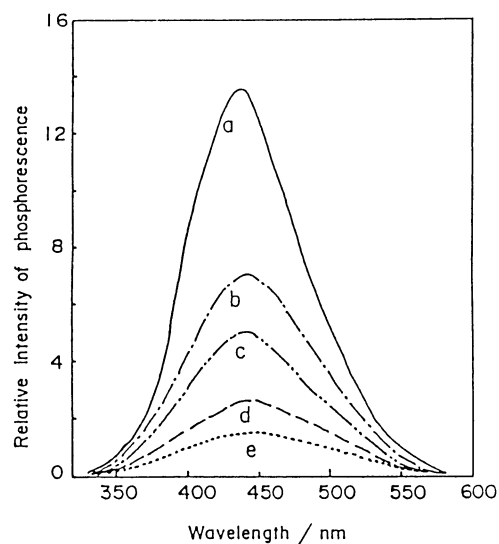


Fig. 1. Phosphorescence of acetone adsorbed on PVG at 77 K. (excitation; 280 nm, adsorbed acetone; 2.8  $\mu$ mol, added NO (in Torr); a; 0, b: 0.49, c: 0.91, d: 2.02, e: 4.04)

Bronsted acidity of the latter is known to be much higher than that of the former.<sup>9)</sup>

UV irradiation of acetone (or acetone-d<sub>6</sub>) adsorbed on deuterated PVG was found to lead the H-D exchange reaction with surface OD (or OH) groups. In Fig. 2, an increase in the optical density of IR absorption spectra of surface OH groups (around 3746 cm<sup>-1</sup>) is plotted against the reaction time. It is easily seen that the H-D exchange reaction proceeds between surface OD groups and excited state of acetone (solid line). By contrast, with the ground state of acetone the reaction scarcely proceeds (dotted line). It is seen in Table 1, that a large fraction of acetone molecules recovered after UV irradiation consists of CH<sub>2</sub>DCOCH<sub>3</sub> and CHD<sub>2</sub>COCH<sub>3</sub> (or CH<sub>2</sub>DCOCH<sub>2</sub>D). A decrease in the efficiency of exchange reaction with increasing the coverage of acetone might arise from the heterogeneity of surface OH groups.<sup>1,7)</sup> The photo-induced H-D exchange reactions were suppressed by the addition of O<sub>2</sub> or NO. These results, together with those in phosphorescence measurements, clearly indicate that the excited triplets of acetone are closely associated with the observed photo-induced H-D exchange reaction.

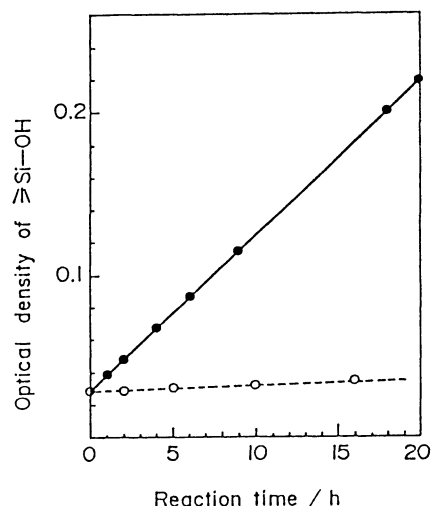


Fig.2. Change of the optical density of Si OH groups vs. reaction time at 295 K. (solid line; photo-reaction, dotted line; dark-reaction, adsorbed acetone; 125  $\mu$ mol/g)

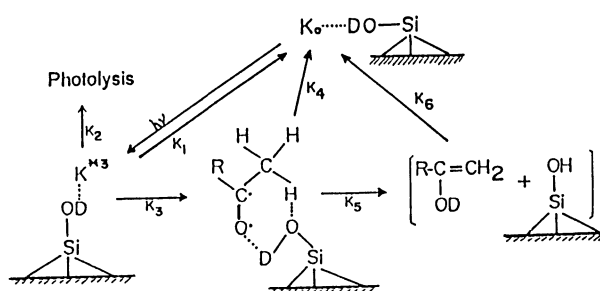
Table 1. Distribution of mono-, di-, and tri-deuterated acetone

Amount of acetone $\mu$ mol/g	Conversion % (5h)	CH <sub>3</sub> COCH <sub>3</sub>	CH <sub>2</sub> DCOCH <sub>3</sub>	CHD <sub>2</sub> COCH <sub>3</sub>	CD <sub>3</sub> COCH <sub>3</sub>
25.4	8.04	91.5	6.25	1.72	0.44
25.4 + NO <sup>a)</sup>	2.80	96.8	2.52	0.43	0.0
25.4 + O <sub>2</sub> <sup>b)</sup>	2.52	97.1	2.21	0.36	0.0
45.1	5.42	94.1	5.00	0.99	trace
117	2.81	96.7	2.50	0.50	0.0

a) Pressure of NO; 6.5 Torr. b) Pressure of O<sub>2</sub>; 2.3 Torr.

As described in our previous papers,<sup>1,7)</sup> the more strongly hydrogen bonded a ketone molecule is, the more efficient radiationless deactivation becomes. Deactivation of acetone was the most efficient in alkyl ketones.<sup>1,7)</sup> It is known that the excited triplet state of alkyl ketones has a high reactivity for hydrogen abstraction reactions.<sup>10)</sup> However, according to Porter et al.,<sup>11)</sup> hydrogen

abstraction, which results in the formation of ketyl radicals, is not an important process in determining the lifetime of excited triplets of acetone in solvents such as water (lifetime = 23  $\mu$ s at 300 K) and acetonitrile (lifetime = 44  $\mu$ s at 300 K), and a chemical pathway for deactivation of the triplet, such as solvent-assisted photoenolization mechanism involving a six-membered intermediate species (vide infra) has been proposed. The results obtained in the present work suggest that a similar deactivation pathway involving surface OH groups-assisted photoenolization plays a decisive role in determining the triplet lifetime of acetone molecules adsorbed on PVG by hydrogen bonding. Thus, the following reaction scheme could be drawn to show the fate of excited triplets of acetone adsorbed on PVG by a hydrogen bonding. Much higher reactivity of surface OH groups on PVG for the excited triplet acetones than that of H<sub>2</sub>O could lead to more efficient photoenolization as well as more efficient deactivation of the excited triplets of acetone (lifetime = 6.7  $\mu$ s at 77 K and less than 1  $\mu$ s at 300 K).



Deactivation pathways of the excited triplets of acetone and H-D exchange reaction on deuterated surfaces of PVG. ( $K_0$  and  $K_0^*$ ; ground state and excited triplet state of acetone, R; CH<sub>3</sub> group)

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#### References

- 1) Y. Kubokawa and M. Anpo, *Hyomen*, 16, 463 (1978), and references therein.
- 2) H. Hada, *Kagaku*, 38, 770 (1983).
- 3) T. Matsuura, *Kagaku*, 41, 752 (1986).
- 4) For example, R. K. Bauer, P. de Mayo, W. R. Ware, and K. C. Wu, *J. Phys. Chem.*, 86, 3781 (1982), and P. de Mayo, A. Safarzaheh-Amire, and S. K. Wang, *Can. J. Chem.*, 62, 1001 (1984).
- 5) N. J. Turro, X. G. Lei, and C. C. Cheng, *J. Am. Chem. Soc.*, 107, 5824 (1985).
- 6) H. Aoyama, K. Miyazaki, M. Sakamoto, and Y. Omote, *Chem. Lett.*, 1983, 1583.
- 7) M. Anpo, T. Wada, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, 50, 31 (1977), and earlier series of Photochemistry in the Adsorbed Layer. (I- VII).
- 8) M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, 92, 258 (1970).
- 9) M. J. D. Low and N. Ramasubramanian, *J. Phys. Chem.*, 71, 730 (1967).
- 10) For example, M. Anpo and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, 50, 1913 (1977).
- 11) G. Porter, R. W. Yip, J. M. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, 67, 3149 (1971), and G. Porter, S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, 69, 1462 (1973).

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