CHEMISTRY LETTERS, pp. 1583-1586, 1983.

PHOTOCHEMICAL REACTIONS OF N,N-DIALKYL α-OXOAMIDES ADSORBED ON SILICA GEL AND ALUMINA

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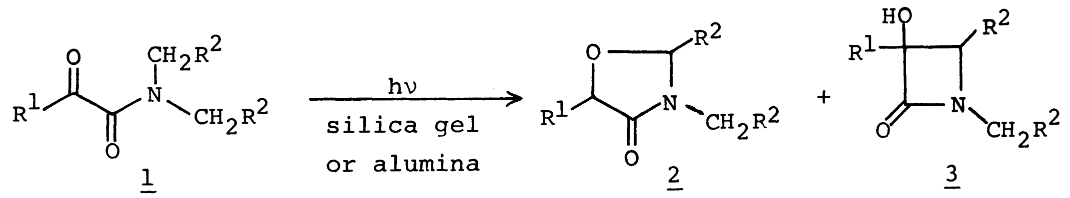
The photochemical reactions of N,N-dialkyl α-oxoamides adsorbed on silica gel were similar to those in acidic methanol, which indicated that the acidity of silanol groups on the surfaces of silica gel played important roles. The photolysis of the amides on alumina resembled those in methanol. The results of the photoreactions also suggested the absence of strong constraint upon the molecular motions of the amides adsorbed on these adsorbents.

Photochemical reactions of organic compounds adsorbed on silica gel or alumina have received much attention.[1-4] It was reported that the adsorption constrained the molecular motions of reactants severely and affected the product distribution in the photoreactions.[1,2] Most of these studies have been concerned with photodecompositions via radical pair intermediates, and the effects of silanol groups of the silica gel surfaces on the photoreactions have been scarcely studied. This is presumably due to the fact that photoreactions are usually not sensitive to the proticity or acidity of the reaction media. Recently, we reported the photochemical reactions of α-oxoamides (1), in which oxazolidinones (2) and β-lactams (3) were obtained as main products.[5] The ratio of the two products varied remarkably with the reaction media (protic or aprotic, and acidic or basic). Furthermore, the yields of the β-lactams became high when the molecular motions of the amides were restricted.[6] Therefore, the photoreactions of these amides are presumed to provide a useful probe for the effects of the adsorbents on photochemical reactions. This paper reports photoreactions of the α-oxoamides adsorbed on silica gel and alumina.

The photolysis on dry silica gel was carried out in the presence of air at room temperature,7) and the results are summerized in Table together with those of the photoreactions in solution. Photolysis of N,N-dialkylpyruvamides (1a and 1b) gives the corresponding β-lactams (3a and 3b) only when the molecular motions of the amides are restricted (e.g. when included in crystals of desoxycholic acid),6b) whereas the amides affords the oxazolidinones (2a and 2b) exclusively on irradiation in solution.5b) As Table 1 shows, the β-lactams were not formed in the photolysis of the amides on silica gel, and the products were the oxazolidinones8) as in the case of the photolysis in solution. This result suggests that the restriction on the molecular motions of the amides adsorbed on silica gel is not severe. This is consistent with the results of studies by de Mayo et al.3) They reported that the rotational motions of molecules adsorbed on silica gel were not suppressed. The photoreactions of N,N-dibenzyl α-oxoamides (1c and 1d) are sensitive to the acidity of the reaction media, and the yields of the oxazolidinones (2c and 2d) increase significantly in the photolysis in acidic solutions.5a) The yields of 2 and 3 in the photolysis of these amides on silica gel were in excellent agreement with those in the photolysis in acidic methanol solutions (Table 1). This results clearly shows that the acidity of silanol groups on silica gel surfaces plays important roles in the photoreactions.



The photolysis of the amides on dry basic alumina (activity I)9) was performed as in the case of that on silica gel. The yields of 2 and 3 in these reactions were low (Table 1). The low yields were found to be due to decomposition of the products during irradiation. Deactivation of the alumina by addition of water (15%, activity V) did not alter the results of the photolysis. Also in this case, the β-lactam (3b) was not formed in the photolysis of 1b. This may be also interpreted as an indication of the absence of strong restriction on the molecular motions of 1b in these conditions. The photolysis of the dibenzylamide (1c) on alumina gave both the oxazolidinone (2c) and the β-lactam (3c). Since 1c gives only 3c on irradiation in aprotic solvents or methanol containing sodium methoxide,5a) the formation of 2c in the photolysis on the alumina indicates that the surfaces of the basic alumina are protic10) and the basicity of the surface is not strong enough to affect the photoreaction of 1c.

In conclusion, the molecular motions on silica gel or alumina are presumed not to be suppressed severely, and the intramolecular photoreactions on dry silica gel are quite similar to those in acidic methanol solution, while the photoreactions on alumina resemble those in methanol to some extent.

Table 1.

Starting materials	Reaction conditions	Reaction time/h	Yield/%	
			2	3
1a: R^1=Me, R^2=H	in MeOH[11)]		>24	0
	on silica gel	7	32	0
1b: R^1=R^2=Me	in MeOH[5a)]		100	0
	on silica gel	15	26	0
	on alumina	20	28	0
1c: R^1=Me, R^2=Ph	in MeOH[5a)]		43	54
	in MeOH-MeONa (0.1M)[5a)]		0	87
	in MeOH-AcOH (5%)[5a)]		84	≈0
	on silica gel	8	72	0
	on alumina	15	12	11
1d: R^1=R^2=Ph	in MeOH[5a)]		0	86
	in MeOH-AcOH (5%)[5a)]		48	37
	on silica gel	5	48	40
	on alumina	8	0	20

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7) Merck Kieselgel 60 (Art. 7734) was used as received. The α-oxoamide (1, 300 mg) was dissolved in hexane or hexane-chloroform (150 ml), and the silica gel (30 g) was added. The solvent was removed under reduced pressure using a rotary evaporator. The resulting sample was placed on a clean glass plate, and irradiated with a 300 W high pressure mercury lamp (Eikosha) for 5-15 h with occasional mixing. The products were washed from the surface with ethyl acetate and purified by flash chromatography on silica gel.

8) The low yields are presumed to be due to the volatility of the starting materials and the products. They may be lost during irradiation. However, the absence of the β-lactams (3a and 3b) in the photoproducts can not be attributed to the volatility of the lactams because they are much less volatile than the oxazolidinones (2a and 2b).

9) Merck Aluminiumoxid 90 aktiv, basisch (Art. 1076) was used as received.

10) The surfaces of aluminas for chromatography are presumed to be covered with hydroxyl groups: H. Rössler, "Thin layer Chromatography. A Laboratory Handbook", E. Stahl Ed., Translated in English by M. R. F. Ashworth, Springer-Verlag, Berlin (1969), pp. 23-27.

10) K. Shima, S. Furukawa, and K. Tanabe, 40th National Meeting of the Chemical Society of Japan, October, 1979, Fukuoka. They reported that photolysis of 1a in methanol gave 2a, a methanol adduct, and an unidentified product in a ratio, 24:55:21.

(Received July 18, 1983)