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Catalysis Utilizing Photo-Energy. I. Specific Photolysis of Phenyl Acetate by Excited Pyridine Catalysis*,[1]

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Irradiation of phenyl acetate in aqueous pyridine gave phenol and acetic acid, both in quantitative yields, in an interesting contrast to the photolysis in aqueous methanol in the absence of pyridine giving photo-Fries rearrangement products mainly. Analysis of the results indicated that by irradiation pyridine accelerated the hydrolysis of phenyl acetate by 120 fold and the quantum yield of the hydrolysis was found to be 0.17.

The present catalysis (acceleration and pathway-control) is interpreted by enhanced nucleophilic and/or general base catalysis of excited pyridine.

It is known on the spectroscopic[3] or theoretical[4] ground, that a photo excited state, especially an excited singlet has considerably different polar character from that of a ground state, as is typically shown by the remarkably increased dissociation constant of excited singlet phenol[5] ($\Delta pKa = pKa^{S_1} - pKa^{S_0} = -6$) or 2-naphthylammonium ($\Delta pKa = -6.1$) as well as by the remarkably decreased dissociation constant of excited singlet benzoic acid ($\Delta pKa = 5.3$) or acridinium ($\Delta pKa = 5.1$). In our current study to utilize the energy of photon as the chemical energy, we have found that some hydrolyses were effectively catalyzed by excited molecules. In this communication, we wish to report the ester hydrolysis catalyzed by an excited pyridine molecule.

It was reported that the photolysis of phenyl acetate gave phenol (28%), acetic acid (not determined),[6] *o*-(19%) and *p*-acetylphenol (15%) in anhydrous ethanol, the latter two are known as the photo-Fries rearrangement products.[8] The photo-Fries rearrangement (*o*-38% and *p*-9%) was also observed in aqueous methanol by the authors (see run 1, Table). In an interesting contrast to the above reactions, the photo-Fries rearrangement of phenyl acetate was found to be completely inhibited in the aqueous pyridine (see run 3, Table).

Thus, phenyl acetate dissolved in aqueous pyridine or in aqueous methanol (with or without addition of KH_2PO_4-$Na_2B_4O_7$) was irradiated with a low pressure mercury lamp. The results are summarized in Table. In the present condition the only products obtained were phenol and acetic acid (both in quantitative yields based on the phenyl acetate reacted). In aqueous pyridine, the calculated ratio of excitation probabilities of phenyl acetate to

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* Dedicated to the memory of Prof. Eiji Ochiai.

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[3] *a*) W. Bartok, R.B. Hartman, and P.J. Lucchesi, *Photochem. and Photobiol.*, **4**, 499 (1965); *b*) E.L. Wehry and L.B. Rogers, *Spectrochim. Acta.*, **21**, 1976 (1965).

[4] J. Del Bène and H.H. Jaffé, *J. Chem. Phys.*, **49**, 1221 (1968).

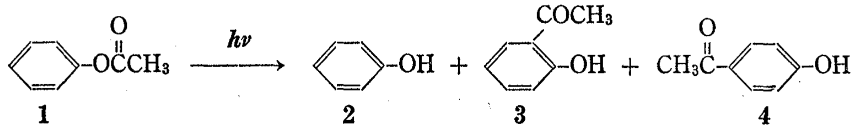
[5] E.L. Wehry and L.B. Rogers, *J. Am. Chem. Soc.*, **87**, 4234 (1965).

[6] The fate of the acetyl group (radical or cation) was obscure. The formation of a trace amount of aromatic aldehyde was reported in the photolysis of phenyl ester of aromatic carboxylic acid.[7]

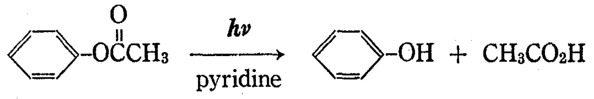
[7] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

[8] *a*) J.C. Anderson and C.B. Reese, *J. Chem. Soc.*, 1781 (1963); *b*) J.W. Meyer and G.S. Hammond, *J. Am. Chem. Soc.*, **94**, 2219 (1972); *c*) C.E. Kalmus and D.M. Hercules, *J. Am. Chem. Soc.*, **96**, 449 (1974).

pyridine was *ca.* 1/600 based on their concentrations used and their molar absorption coefficients. Since most of the light irradiated was absorbed by the solution under the present conditions, the number of the directly excited phenyl acetate molecules in run 3 was only *ca.* 1/600 compared with that in run 1. However, the phenol formation was quantitative in aqueous pyridine, the amount of which was 120 times as large as that expected from the directly excited phenyl acetate, on the basis of the conversion observed and the expected fraction of the direct excitation, after making necessary corrections to the dark hydrolysis by pyridine. Therefore, the present specific and accelerated photo hydrolysis in aqueous pyridine was not due to the direct reaction of excited phenyl acetate.



(1a)



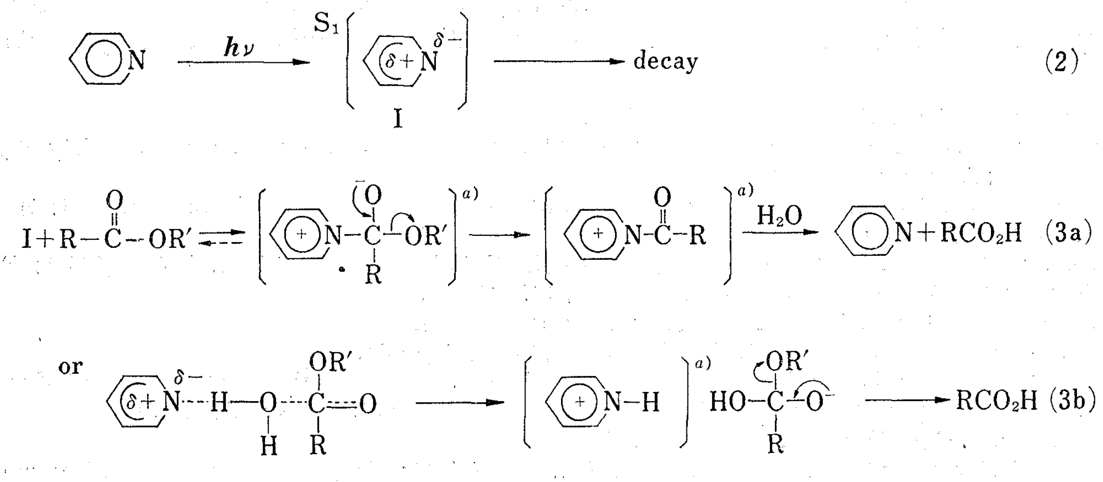
(1b)

Table I

	condition			compound (%) 1	2	3	4
run 1	methanol–water (3 : 1 by volume)	$h\nu$[a)]	375 min	40	13	38	0
		dark[b)]	3000 min	100	trace	0	0
run 2	methanol–phosphate buffer, pH 8.8 (3 : 1 by volume)	$h\nu$[a)]	300 min	20	23	29	28
		dark[b)]	220 min	51	49	0	0
run 3	pyridine–water[c)] (1 : 4 by volume)	$h\nu$[a)]	360 min	86±0.5	14±0.5	0	0
		dark[b)]	360 min	97.5	2.5	0	0

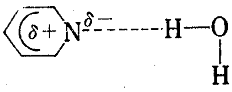
a) at *ca.* 17°
b) at room temperature
c) averaged value of 3 independent experiments

Thus, a conclusion is drawn that the excited pyridine catalyzed the hydrolysis of the ground phenyl acetate remarkably. Plausible mechanisms are shown in chart. The mechanism 3b, involving excited pyridine as a general base, seems to be more plausible than the direct nucleophilic attack of exited pyridine, mechanism 3a. The photohydration of the



Schema

a) either excited or ground

type  followed by the ring opening was reported elsewhere.[9] Calculations were also carried out on π-electron densities of some heterocyclics, pyridine, quinoline, and acridine, by use of the VI/1 method,[10] a kind of self consistent field (SCF) treating π-electron only, and the results were summerised below. This result indicates that among a series of heterocyclics, pyridine is expected to be themost promising candidate for the photocatalysis.

	p*K*a obs.	π-electron density at N atom		
		ground state	1 st excited state	2 nd excited state
pyridine	5.23	-0.262	-0.431	
quinoline	4.94	-0.290	-0.373	
acridine	5.50	-0.356	-0.276	-0.404
(energy differentce between excited and ground state, eV)			(3.66)	(3.77)

Quantum yield of phenol in run 3 was determined by the actinometry[11] to be 0.17 based on the quanta aborbed by the system, or 102 based on the quanta absorbed by phenyl acetate. This is again in accord with the previous conclusion of the excited pyridine catalysis.

The present results indicate that the photon energy can be very effectively utilized (at least in principle) to the promotion of catalysis, *i.e.*, acceleration and/or control of reaction pathway by the irradiation.

Experimental Section

Photolysis in Aqueous Pyridine——A solution of 3.0 g of phenyl acetate dissolved in pyridine (100 ml) and water (400 ml) was irradiated with a 100 W low pressure mercury lamp. The lamp was immersed into the solution and the irradiation was carried out under nitrogen. The solution was thermostated at *ca.* 17° during the irradiation by external cooling with ice. After irradiation for 6 hours, the solution (10 ml) was acidified and extracted with ether (80 ml) three times. The ether extracts were combined and washed with a saturated solution of sodium chloride (50 ml) twice and dried over sodium sulfate. The careful fractional evaporation of the ether layer gave a viscous liquid, which consisted of phenol **2** (14%), acetic acid and recovered phenyl acetate **1** (86%) on the basis of gas-liquid partition chromatography (GLPC) glpc analysis. Structures of these compounds were determined by comparison of their GLPC and infrared (IR) spectra with those of authentic samples. The results are shown in Table. The formation of phenol and acetic acid in irradiated aqueous pyridine was found to be quantitative by use of acetophenone as an internal standard[12] for GLPC glpc analysis. The formation of phenol in the photo reaction was followed at appropriate intervals, and the amount of phenol thus formed was found to increase almost linearly with time up to 6 hours irradiation.

Some dark reactions (treatment of phenyl acetate with aqueous pyridine) were carried out under corresponding condition for calibration.

Photolysis in Aqueous Methanol with Addition of KH_2PO_4-$Na_2B_4O_7$——A solution of 3.0 g of phenyl acetate dissolved in methanol (375 ml) and phosphate buffer at pH 8.8 (125 ml) was irradiated as described above. Similar treatments of the irradiated solution gave a liquid which consisted of phenol **2** (23%), *o*-acetylphenol **3** (29%) and *p*-acetylphenol **4** (28%) based on GLPC analysis. Structures of these compounds were determined by comparison of their GLPC and IR spectra with those of authentic samples.

Again, dark reaction was carried out under corresponding condition for calibration. The results are shown in run 2 of Table.

Photolysis in Aqueous Methanol——A solution of 3.0 g of phenyl acetate dissolved in methanol (375 ml) and water (125 ml) was irradiated as described above. After irradiation for 6 1/4 hours, the solution was extracted with ether three times. The products thus obtained consisted of phenol (13%), *o*-acetylphenol (38%) and *p*-acetylphenol (9%) together with the recovered acetate (40%). Similar treatments as described above gave result as shown in Table.

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9) J. Joussot-Bubieu and J. Houdard, *Tetrahedron Letters*, **1967**, 4389.
10) T. Kobayashi and Z. Yoshida, *Theoret Chim. Acta*, **19**, 377 (1970).
11) C.G. Hatchard and C.A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).
12) Before analysis, a given amount of acetophenone was added to the solution to be determined.

Dark reaction was carried out under identical conditions for comparison. The results are shown in run 1 of Table.

Measurement of Quantum Yield ϕ——To measure the quantum yield of the hydrolysis of phenyl acetate in aqueous pyridine, repeated photolyses were carried out in a two-component quartz cell with optical path of 5 and 10 cm, respectively, by irradiation from the outside of the cell with a 100 W low pressure mercury lamp. The temperature of the solution was maintained at room temperature by external cooling with air. The front cell (close to the lamp) of 5 cm length was filled with 35 ml of the aqueous pyridine solution and the rear cell (apart from the lamp) of 10 cm length was filled with a solution of chemical actinometer including potassium ferroioxalate (70 ml). Numbers of quanta were measured by this chemical actinometer both for aqueous pyridine and for phenyl acetate dissolved in aqueous pyridine. The number of quanta absorbed was practically not affected (within 2.5%) by the addition of phenyl acetate to aqueous pyridine.13) Thus, the number of quanta absorbed by the system was estimated as a difference between measured quanta for the cell filled with water and those for the cell filled with the photolysis solution. The number of quanta absorbed by pyridine (Table run 3) was found to be 4.75×10^{-8} einstein/sec, wherefrom quantum yield of the hydrolysis was estimated to be 0.17.

Potassium ferrioxalate $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ for the actinometer was prepared according to the procedure reported by C.G. Hatchard and C.A. Parker.14)

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13) Because the molar ratio of pyridine to phenyl acetate used was $1.24/2.2 \times 10^{-2}$, which means the ratio of excitation probabilities of these compounds amounted to *ca.* 600 : 1.

14) C.A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); see also, J.G. Calvert, and J.N. Pitts, Jr., Photochemistry" John Wiley, New York, 1966, p. 783.