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A Photoreaction of 4-Nitrophenylnitromethane in a Micellar System

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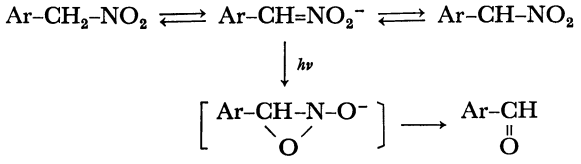
Synopsis. The photoconversion of 4-nitrophenylnitormethane into 4-nitrobenzaldehyde in an ethanol–water system was found to proceed by an intramolecular rearrangement of oxygen of adjacent nitro group. Cationic surfactant increased the quantum yield of this photorearrangement by a factor of 20, but β-cyclodextrin decreased it.

4-Nitrophenylnitromethanide anion is formed in ethanol–water by removal of a proton from 4-nitrophenylnitromethane (**1**). The nitromethanide anion is thermally stable for at least 24 h. The present paper is concerned with its photorearrangement. The catalytic effect of a cationic surfactant and β-cyclodextrin (β-CDX) was also studied.

Photoreaction. Irradiation of a 20% (vol) ethanolic alkaline aqueous solution of **1** gave 4-nitrobenzaldehyde.



$$\text{Ar-CH}_2\text{-NO}_2 \rightleftarrows \text{Ar-CH=NO}_2^- \rightleftarrows \text{Ar-}\bar{\text{C}}\text{H-NO}_2 \xrightarrow{h\nu} [\text{Ar-CH-N-O}^-] \longrightarrow \text{Ar-CH=O}$$

The ionization, removal of a proton from **1**, and the decrease of the aci-nitroate anion of **1** during the course of irradiation followed the pseudo-first-order kinetics. The rate constant of the ionization was greater than that of the decrease under the present conditions.[1] The decrease of aci-nitroate anion is considered to be the rate-limiting step in the overall rate of photoreaction. The photoreaction was followed by ultraviolet spectroscopy. Isosbestic points were found at 312, 256, and 227 nm as the time of irradiation; the maximum absorbance of the aci-nitroate anion of **1** at 384 nm decreased, while a new maximum appeared at 268 nm, the position for $\lambda_{\max}$ of 4-nitrobenzaldehyde.

4-Nitrophenylacetonitrile which has a cyano group instead of a nitro group was photoconverted into 4-nitrobenzaldehyde by oxygen in an ethanol–aqueous alkali solution. It was not allowed to react under anaerobic conditions. The observed quantum yield for the photoconversion of **1**, however, did not change in the presence or absence of oxygen. From these results and the fact that the oxazirane ring decomposes by the action of alkali to the formation of carbonyl compounds[2] it is shown that the photoreaction of **1** proceeds by an intramolecular attack of oxygen on the adjacent nitro group to α-carbon.

TABLE 1. THE EFFECT OF CTAB AND β-CDX ON THE VISIBLE SPECTRA AND THE pK_a VALUE OF 4-NITROPHENYLNITROMETHANE

	H_2O	CTAB[a]	β-CDX[b]
$\lambda_{\max}$/nm[c]	384	404	390
pK_a[d]	6.00	4.92	4.84

a) In the presence of 10^{-2} M CTAB. b) In the presence of 4×10^{-3} M β-CDX. c) In 20% ethanolic aqueous buffer (pH 6.90). d) In 20% ethanolic water at room temperature. The pK_a values were measured according to the method of Wolff.[3]

In order to confirm the mechanism of this photorearrangement, the relation between the stability of the aci–nitroate anion and the photoreaction was studied. The presence of a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and β-CDX caused a red shift in the $\lambda_{\max}$ for the aci-nitroate anion (Table 1). The $\lambda_{\max}$ for 8×10^{-5} M of **1** in 20% (vol) ethanolic aqueous buffer (pH 6.90) began to show the shift at a concentration of CTAB above 2.24×10^{-4} M, which indicates a critical micelle concentration (CMC) of CTAB for **1**.

The presence of CTAB and β-CDX in micellar concentration decreased the pK_a value of **1** (Table 1), indicating the stabilization of aci-nitroate anions This results from (a) electrostatic interaction with cationic head groups of CTAB and the anion form, and (b) electron delocalization by the hydrogen bond between an adjacent hydroxyl group of β-CDX and an oxygen atom of 4-nitro group of the substrate which forms a 1:1 inclusion complex with β-CDX.

The quantum yield for the photoreaction of **1** in 20% ethanolic aqueous buffer (pH 6.90) increased in the presence of micellar concentration of CTAB. The quantum yield started to increase above 1.78×10^{-4} M of CTAB in good agreement with CMC. Since the quantum yield reached saturation in high concentration

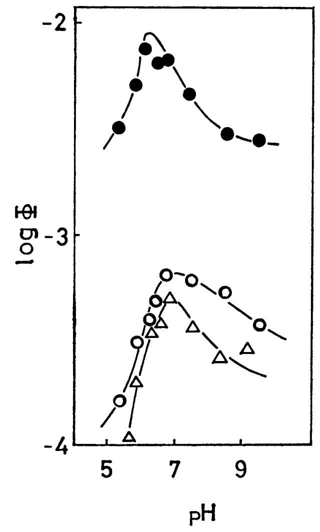


Fig. 1. A pH-quantum yield profile for the photorearrangement of 4-nitrophenylnitromethane. ○: In the absence of surfactants, ●: in the presence of 5×10^{-3} M CTAB, △: in the presence of 4×10^{-3} M β-CDX.

of CTAB, a general mechanism involving the micelle-substrate complex in a manner analogous to that for enzymatic catalysis[4] was applied. Micellar CTAB increased the quantum yield (Φ_{obsd}) for the photoreaction of **1** in 20% ethanolic aqueous buffer (pH 5.38) by a factor of 20, and increased the quantum yield for the formation of product from the micellar phase (Φ_2) by a factor of 12.

Variation of quantum yields over the pH range 5—10 was bell-shaped both in the absence and the presence of CTAB and β-CDX (Fig. 1). When CTAB was present, its maximum moved to a lower pH range. Stabilization of the aci-nitroate anion by CTAB micelle reflects directly on the quantum yield. The difference in OH^- concentration between micellar surface and bulk phase is an important factor. However, no such direct influence of stabilization appeared in the presence of β-CDX. The quantum yields decreased in the presence of β-CDX over all the pH range. Probably the dynamic equilibrium of micell micellar CTAB facilitates the rearrangement of oxygen of adjacent nitro group and the rigid cavity of β-CDX inhibits the rearrangement of substrate forming a complex with β-CDX.

Experimental

UV spectra were taken on a Hitachi ESR-3T or Shimadzu UV-200 spectrometer. The pH value was measured with a model HM-5A pH meter (TOA Electronics, Co., Ltd.). The following buffer solutions were used according to the required pH range: M/15 KH_2PO_4–Na_2HPO_4 (pH 5—9), M/20 H_3BO_3–KCL (pH 9—10), M/20 Na_2HPO_4–NaOH (pH 10—12). Commercial CTAB was recrystallized twice from methanol–ether.[5] Other materials were used without further purification. 4-Nitro-phenylnitromethane was prepared by the procedure of Hantzsch and Veit.[6]

Irradiation of 4-Nitrophenylnitromethane (1). A solution of 500 mg of **1** in 1 liter of ethanol-aqueous NaOH solution was as irradiated with an Ushio UM-452 450 W high pressure mercury lamp for 3 hs. After irradiation, the solvent was removed with a rotary evaporator and the oily residue was chromatographed on silica gel using hexane: benzene mixture as an eluent to give two products. The first product (90 mg) seemed a dimer-like compound, mp 286—290 °C, and MS, *m/e* 270 (M^{+}). No further effort has been made to determine the structure. The second product (20 mg) was identified as 4-nitrobenzaldehyde.

4-Nitrobenzoic acid analysis was carried out by high speed liquid chromatography with a Hitachi Liquid Chromatograph 634A equipped with a UV monitor. Hitachi gel #3020 was packed into the column (2.1φ × 500 mm) with a mobile phase of the mixture of methanol–water (8: 2) system. The flow rate of the phase 0.85 ml/min. with a column pressure of approximately 80 kg/cm^2. The column temperature was 50 °C. Under these conditions, the retention volume of 4-nitrobenzaldehyde and 4-nitrobenzoic acid was 3.06 ml and 1.79 ml, respectively. Variation of the concentration of 4-nitrobenzoic acid with the time of irradiation of **1** was obtained. The formation of 4-nitrobenzaldehyde was slow as compared with the photoreaction, giving no effect on the kinetics.

Kinetic Method. The kinetics was studied by following the reaction spectrophotometrically at the λ_{max} of the nitronate anion in each buffer solution at room temperature. All the data were treated as those of pseudo-first-order kinetics. The estimated rate constant values were converted into the the quantum yield.[7]

Effect of Dissolved Oxygen on the Reaction. After bubbling argon gas for a certain time in order to remove dissolved oxygen, the solution was irradiated and the rate was measured. The quantum yield obtained was compared with that in the pressure of dissolved oxygen.

References

1) For example, the k_{obsd} value for the ionization was 2.47×10^{-2} s^{-1} and that for the photoreaction was 5.41×10^{-5} s^{-1} in 20% (vol) ethanolic aqueous buffer (pH 6.90) at 15 °C. Avery and Bultler reported that the k_{obsd} for the ionization of **1** at zero buffer concentration is 5.75×10^{-3} s^{-1} in 1% dioxanborax buffer at pH 8.10 and 25 °C: S. P. Avery and A. R. Bultler, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1110.

2) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

3) M. J. Minch, M. Giaccio, and R. Wolff, *J. Am. Chem. Soc.*, **97**, 3766 (1975).

4) J. H. Fendler and E. J. Flendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975).

5) E. F. J. Duynstee and E. Grunwald, *J. Am. Chem. Soc.*, **81**, 4540 (1959).

6) A. Hantzsch and A. Veit, *Ber.* **32**, 607 (1899).

7) K. Yamada, S. Kohmoto, and H. Iida, *Bull. Chem. Soc. Jpn.*, **49**, 1171 (1976).