

Preliminary Note

Studies on the photoreaction of heterocyclic *N*-dioxides: photoreaction of pyrazine *N*-dioxide in aqueous solution

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(Received February 4, 1980)

Pyrazine monoxides are known to undergo photoreaction to produce 2-hydroxypyrazine in polar solvents via the oxaziridine intermediate [1]. However, the photoreaction of pyrazine *N*-dioxide has not been studied. In this work we report on the photochemical reaction mechanism of pyrazine *N*-dioxide in protic solvents. An attempt was made to identify the photoproduct.

The change in the electronic spectrum of pyrazine *N*-dioxide (PD) with UV light illumination* in aqueous neutral solution is shown in Fig. 1. The absorption of the product at 266 nm increases with the illumination time at the expense of the absorption of PD at 307 nm. An isosbestic point appears at 283 nm. Deaeration of the solutions has no effect on the spectral change and the reaction rate. The photoproduct decomposes thermally with a rate constant of $2.10 \times 10^{-5} \text{ s}^{-1}$ at 25 °C in both aerated and deaerated solutions. The reaction in ethanol is similar to that in aqueous solution.

In the IR absorption spectrum (KBr) of the photoproduct, the band at 1300 - 1305 cm^{-1} found for pyrazine monoxide [2] was not observed. Instead, a broad band at about 3200 cm^{-1} was observed which can be assigned to the —OH stretching vibration. Thus the two N→O groups of PD are thought to be modified by the photoillumination. No proton nuclear magnetic resonance signal of the photoproduct was observed when a D₂O solution was illuminated; this implies that the photoproduct has a structure

*The light source was a 100 W high pressure mercury lamp (Toshiba SHL-100UV) with a Pyrex filter which eliminated irradiation wavelengths shorter than 280 nm.

in which all the hydrogen atoms are readily exchangeable for deuterium atoms.

The effect of light intensity on the reaction rate was investigated. Figure 2 gives a plot of $\ln k$ (k is the rate constant of the photochemical first order reaction*) versus $\ln I$ (I is the relative light intensity) for an aqueous solution at 25 °C. The slope of the straight line is 1.88. Thus, because the reaction rate is proportional to the square of the light intensity, the photo-reaction must involve a biphotonic process.

On the basis of the results obtained, we propose the mechanism shown in Scheme 1.

The first and the second steps are similar to those of the photochemical reaction mechanism for pyrazine monoxide [1]. The first photon absorbed is used for the conversion of an oxygen atom of an N→O group into —OH at a position adjacent to the original N→O group, whilst the second photon changes the oxygen atom of the remaining N→O group into —OH at a position adjacent to the second N→O group. Two processes, process [I] and process [II], are possible, depending on the position of the second —OH group relative to the first. Since oxygen in solution does not affect the reaction and no intermediate species is observed using ordinary flash photolysis experiments, the photoreactive species are considered to be the excited singlet species of 1 and 3.

The exchange of all hydrogen atoms of the photoproduct with deuterium atoms can be explained by keto-enol tautomerism of the intermediate 3

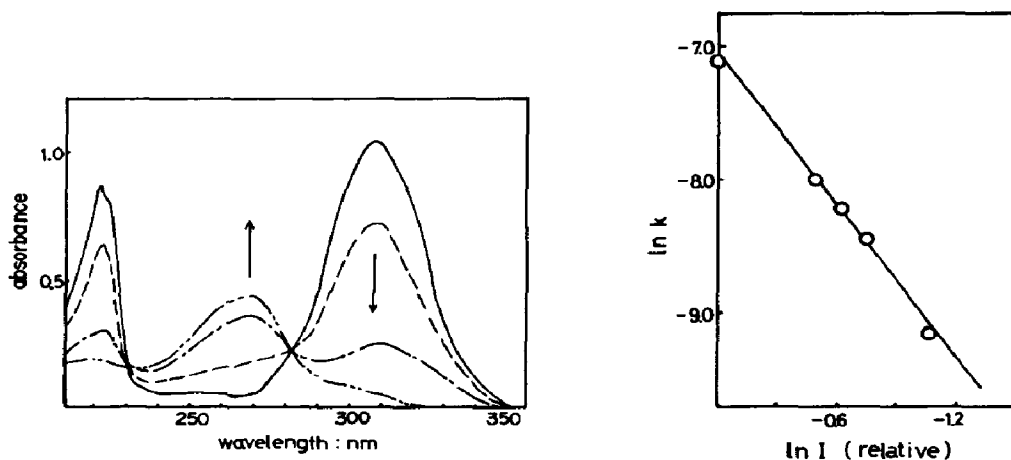
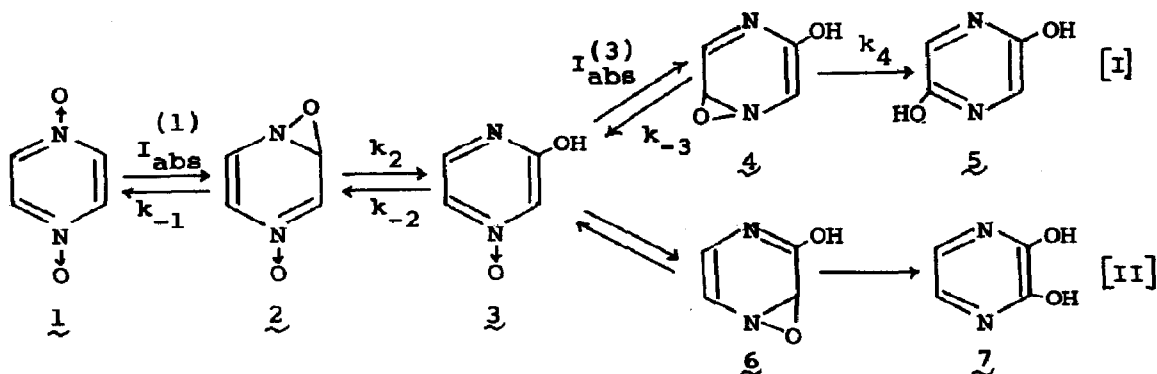


Fig. 1. The change in the electronic spectrum of PD with UV light illumination in aqueous neutral solution: —, before illumination; ---, after illumination for 90 s; - · - · -, after illumination for 150 s; · · · · ·, after illumination for 420 s.

Fig. 2. The effect of light intensity on the reaction rate.

* k was obtained [3] from the slope of a plot of $\ln(e^{2.303kA} - 1)$ versus t , where A is the absorbance of the reactant at 313 nm and t is the time.



Scheme 1. The proposed photochemical reaction mechanism for PD.

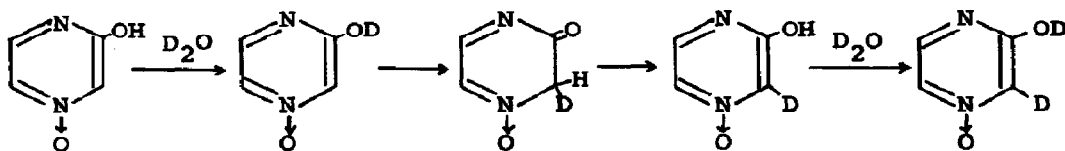
and/or of the product 5 (Scheme 2). Process [II] is excluded because all the hydrogen atoms are not exchangeable.

Detection of the hydroxyl group, which is a possible functional group formed in this reaction, was carried out by the potassium ferricyanide–ferric chloride method [4] for the aqueous solution. The existence of the hydroxyl group was confirmed by the blue colouration of the test solution. Consequently the photoproduct was identified as 2,5-dihydroxypyridazine.

The biphotonic process is discussed briefly in terms of process [I]. Since all the intermediates are considered to have very short lifetimes, the steady state approximation can be applied. If the light absorption rate is $I_{abs}^{(i)}$ and the rate constants are k_i , as indicated in process [I], the rate of disappearance $-d[PD]/dt$ of PD is represented by the following equation:

$$-\frac{d[PD]}{dt} = \frac{2.303\epsilon_3\gamma_2\gamma_4I^2}{2.303\epsilon_3\gamma_4I + k_{-2}(1 - \gamma_2)} (1 - e^{-2.303\epsilon_1[PD]})$$

where $I_{abs}^{(1)} = I(1 - e^{-2.303\epsilon_1[PD]})$, $I_{abs}^{(3)} = 2.303\epsilon_3I[3]$, ϵ_i is the molar extinction coefficient of species i , $\gamma_2 = k_2/(k_{-1} + k_2)$ and $\gamma_4 = k_4/(k_{-3} + k_4)$. If the condition $2.303\epsilon_3\gamma_4I \ll k_{-2}(1 - \gamma_2)$ holds, then $-d[PD]/dt \propto I^2$. This condition is fulfilled. The proportionality constant is $(2.303)^2\epsilon_1\epsilon_3\{k_2/k_{-1}k_{-2}\}\{k_4/(k_{-3} + k_4)\}$ for low PD concentrations. Thus the proposed mechanism [I] (especially the existence of the processes k_{-1} and k_{-2}) seems to be plausible from the kinetic analysis.



Scheme 2. The keto–enol tautomerism of the intermediate 3.

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