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A MECHANISM OF THE PHOTOCHEMICAL ISOMERIZATION OF QUINOLINE N-OXIDES

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The photochemical behavior of 2-cyanoquinoline N-oxide and 4-methylquinoline N-oxide in aqueous ethanol containing potassium iodide or ethyl iodide was examined. The results indicate that Process I (N-oxide → lactam) proceeds via a protonation of the N→O group through a hydrogen-bonding interaction in the S_1 state, whereas Process II (N-oxide → oxazepine) occurs with the formation of oxaziridine intermediate from the S_1 state.

In a previous paper,[1)] the photochemical isomerization of azanaphthalene N-oxides, such as quinoline N-oxide and isoquinoline N-oxide, arising from the excited singlet state (S_1) has been demonstrated to be closely related to whether or not the N-oxide oxygen atom forms a hydrogen bond with a solvent molecule; that is, such a hydrogen bond formation is essential for the photochemical rearrangement to the lactam (Process I), but not for the photoisomerization into the oxazepine (Process II). In addition, Process I has been assumed to proceed via a protonation of the N→O group through hydrogen-bonding interaction in the S_1 state (Scheme 1), whereas Process II occurred with the formation of oxaziridine intermediate from the S_1 state (Scheme 2). According to the mechanism as shown in Scheme 1 or 2, iodide ion can be expected to act as a reductant for the oxaziridine in Process II[1)] and as a quencher for the excited singlet protonated N-oxide in Process I,[2)] while ethyl iodide appears to function as a heavy atom quencher for the excited singlet species in either Process I or II. Therefore, the present authors examined the photochemical behavior of 2-cyanoquinoline N-oxide and 4-methylquinoline N-oxide in aqueous ethanol in the presence of potassium iodide or ethyl iodide at room temperature,[3)] and discussed the mechanism of the photochemical isomerization of azanaphthalene N-oxides into lactam or oxazepine.

2-Cyanoquinoline N-Oxide. Irradiations of 2-cyanoquinoline N-oxide in 95% ethanol resulted in Process II to give the oxazepine in ca.90% yield, but Process I was not induced because of the lack of a hydrogen-bonding interaction between the N→O group and the solvent molecule. The deoxygenation product (2-quinolinecarbonitrile) originated from the lowest triplet state (T_1) was obtained in ca.10% yield.

In Fig.1, the quantum yields of the photochemical reaction of 2-cyanoquinoline N-oxide at 313 nm were plotted against the concentration of iodide ion ($[I^-]$) in deaerated 95% ethanol. As can be seen from the figure, the quantum yield of the formation of oxazepine (Φ_{oxa}) decreased and that of the formation of deoxygenation product (Φ_{deo}) increased with an increase of $[I^-]$, although the quantum yield of the disappearance of N-oxide (Φ_{dis}) was independent of $[I^-]$. In addition, a large amount of iodine was also found to be liberated.[1] Curve (a) in Fig.2 shows the Stern-Volmer plot for Φ_{oxa}, from which the quenching constant ($k_q\tau$) was evaluated to be 1.71 X 10^3 M^{-1}. Assuming the quenching reaction to be diffusion-controlled (k_q = 4.63 X 10^9 $M^{-1}s^{-1}$), the lifetime of intermediate species (τ) in the absence of iodide ion was estimated to be 0.37 μs, which approximately agreed with the lifetime of a possible oxaziridine intermediate (<4 μs).[4] On the other hand, the quantum yields were unaffected by ethyl iodide, indicating that the intersystem crossing from the S_1 state of the N-oxide is not sensitive to an external heavy atom effect. These results lead to the conclusion that the photoisomerization proceeds via an oxaziridine intermediate which is reduced by the iodide ion to give the deoxygenation product. Also, the facts that 2-cyanoquinoline N-oxide is non-fluorescent and its photochemical behavior (singlet reaction) is not affected by heavy atom quencher imply that the formation of oxaziridine intermediate from the S_1 state takes place rapidly with a rate of 10^{10}– 10^{11} s^{-1} as in the case of photoisomerization of α,N-diphenylnitrone to oxaziridine.[5] Thus, it seems to be undoubted that Process II proceeds according to the mechanism as shown in Scheme 2.

4-Methylquinoline N-Oxide. 4-Methylquinoline N-oxide in 95% ethanol underwent preferentially photochemical rearrangement to the lactam (ca.70% yield) through a hydrogen-bonding interaction between the oxygen atom of N→O group and the solvent molecule, and concurrently Process II also occurred to some extent to give the oxazepine which was too unstable to isolate. The deoxygenation product (4-methylquinoline) originated from the T_1 state was obtained only in traces.

In Fig.1 also shown are the quantum yields for the photochemical reaction of 4-methylquinoline N-oxide at 313 nm as a function of $[I^-]$ in deaerated 95% ethanol. As can be seen from the figure, the quantum yield of the formation of lactam (Φ_{lac}) decreased and that of the formation of deoxygenation product (Φ_{deo}) increased with an increase of $[I^-]$, whereas the quantum yield for the disappearance of N-oxide (Φ_{dis}) was independent of $[I^-]$. Differing from the case of 2-cyanoquinoline N-oxide, however, appreciable amounts of iodine were not liberated. As shown by curve (b) in Fig.2, the Stern-Volmer plot for Φ_{lac} was linear with a slope of $k_q\tau$ (1.42 X 10 M^{-1}), from which the lifetime of intermediate species (τ) in the absence of iodide ion was estimated, by assuming the quenching as a diffusion-controlled reaction, to be 3.1 ns. On the other hand, the quantum yields were scarecely affected by ethyl iodide, indicating that the excited singlet species are not subject to heavy atom quenching as in the case of 2-cyanoquinoline N-oxide. Meanwhile, Aloisi and Favaro have reported that halide anions quench the fluorescence from the protonated quinoline N-oxides accompanying an increase in the phosphorescence intensity[2]; that is, phosphorescence to fluorescence intensity ratio of quinoline N-oxides in acidic solution was observed to increase noticeably by using HBr instead of HCl as an acidifying agent, indicating that the excited singlet protonated N-oxide is quenched by halide anions to the T_1 state. Considering this fact, the experimental results presented above suggest strongly that the photorearrangement of 4-methylquinoline N-oxide to the lactam proceeds via the excited singlet protonated N-oxide, having a lifetime of ca.3.1 ns, which is deactivated by the iodide ion to the T_1 state responsible for the deoxygenation. This is also consistent with a mechanism of Process I proposed in a previous paper.1) Thus, as shown in Scheme 1, the photoexcitation of a hydrogen-bonded N-oxide may be concluded to cause a rapid protonation of the N→O group to give an excited ion-pair through which a conversion to the lactam occurs, although the hydrogen-bonded N-oxide excited into the S_1 state is also responsible for Process II. In this scheme, a possible reaction pathway is probably either Path a or b, but not Path c, since the photochemical conversion of quinoline N-oxide-2-d_1 into the lactam involves the shift of a deuterium from the 2-position of a quinoline nucleus to either the 1- or 3-position6) and also the transfer of a proton from the tertiary carbon site to RO^- in Path c is considered to be difficult energetically.

Further studies are now in progress. The present work was supported by a Grant-in-Aid from the Ministry of Education.

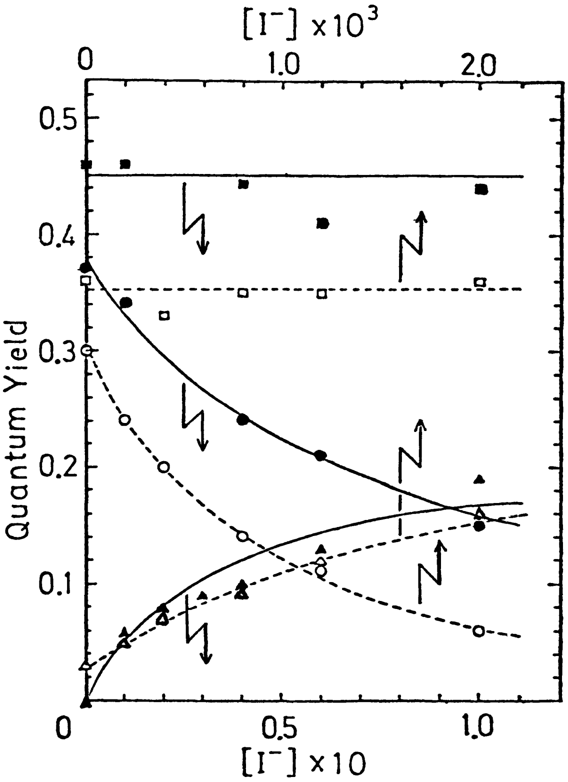


Fig.1 Quantum Yield vs Concentration of Iodide Ion. Solvent : 95% Ethanol, [N-Oxide] = 1.80 X 10^{-3} M.

—— : Φ_{dis}(■), Φ_{lac}(●) and Φ_{deo}(▲) in the photoreaction of 4-methylquinoline N-oxide.

---- : Φ_{dis}(□), Φ_{oxa}(○) and Φ_{deo}(△) in the photoreaction of 2-cyanoquinoline N-oxide.

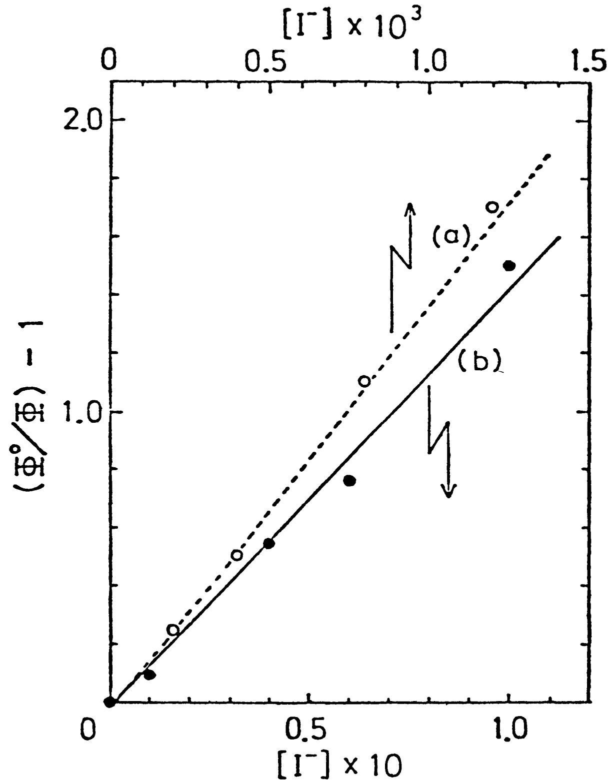
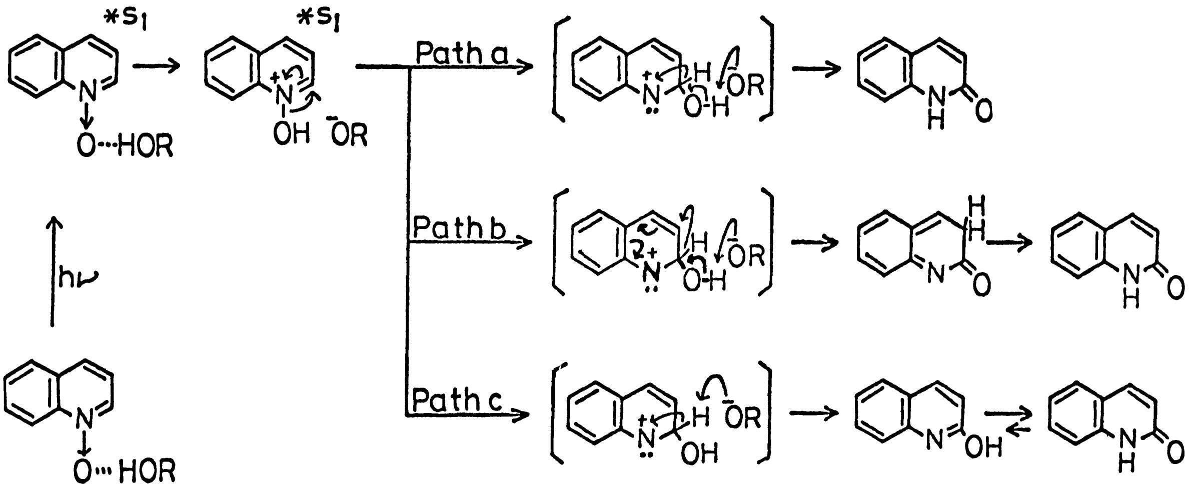
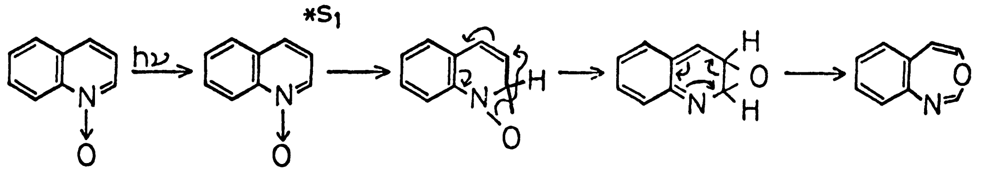


Fig.2 Stern-Volmer Plot.

Scheme 1



Scheme 2



References and Notes

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2) G.G.Aloisi and G.Favaro, J.Chem.Soc.Perkin II, 456 (1976).

3) The photolytic procedure was the same as reported previously.[1] The light source was a 250 W high-pressure mercury lamp (USH-250D) equipped with a filter combination of a nickel sulfate solution with UV-31 and UVD-25 Toshiba filters for the 313-nm irradiation. The photolytic experiment in the presence of ethyl iodide was performed by the 366-nm light, for which UV-D1B and V-V40 Toshiba filters were used.

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