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RADICAL ION PAIR MECHANISM OF THE PHOTOCHEMICAL ISOMERIZATION OF ISOQUINOLINE N-OXIDE IN HYDROXYLIC SOLVENTS, INCLUDING THE MAGNETIC FIELD EFFECT

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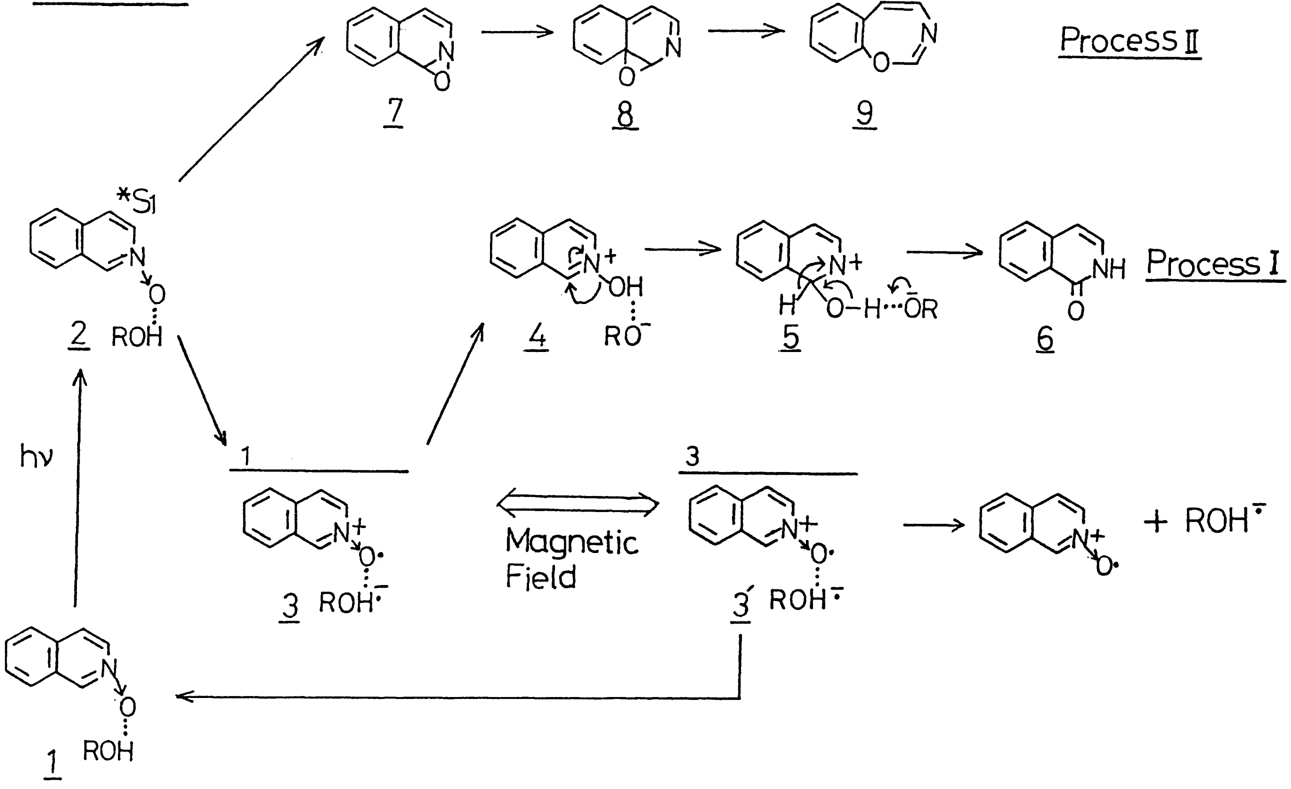
It was found that, while the photochemical isomerization of isoquinoline N-oxide into lactam shows magnetic field effect due to HFI-J mechanism, the N-oxides bearing an electron-donating substituent are insensitive to an external magnetic field. The results support strongly "radical ion pair mechanism" of the photochemical isomerization.

Isoquinoline N-oxide 1 in solution undergoes photochemical isomerization arising from the S_1 state to give the lactam 6 (Process I) and unstable oxazepine 9 (Process II), especially Process I (N-oxide → lactam) occurring predominantly in hydroxylic solvents (ROH).$^{1)}$ In 1976 it has been found that when isoquinoline N-oxide 1 in ethanol was irradiated in the presence of a magnetic field the chemical yield of lactam 6 showed a minimum at approximately 10kG (curve (a) in the Figure).$^{2)}$ In order to account for the magnetic field effect, the reaction was assumed to proceed through an electron transfer followed by hydrogen atom transfer between the excited singlet N-oxide and the hydrogen-bonded solvent molecule (ROH) as shown in the Scheme; hereafter, it is referred to as "radical ion pair mechanism" of Process I. Thus the observed magnetic field effect was reasonably explained on the basis of hyperfine interaction including the exchange interaction in the hydrogen-bonded radical ion pair 3, that is , magnetic field effect due to HFI-J mechanism.$^{3,4)}$ The radical ion pair mechanism was supported by the fact that when isoquinoline N-oxide was irradiated in various alcohols the magnetic field causing a minimum in the yield of lactam was progressively shifted to higher fields with decreasing pK_a of alcohol (pK_a: t-butyl alcohol > 2-propanol ≃ ethanol > methanol).$^{6)}$ In the present communication, we wish to report unexpected observations that the photochemical isomerization of isoquinoline N-oxide bearing an electron-donating substituent (4-Br or 3-CH_3) in ethanol or in t-butyl alcohol is insensitive to external magnetic field.

The experimental procedure was quite similar to that described in previous communications.$^{7)}$ Curves (b) and (c) in the Figure show the results obtained in the case of 4-bromoisoquinoline N-oxide, from which the chemical yield of lactam was proved to be independent of a magnetic field, that is, 56% in ethanol and 41% in t-butyl alcohol. In the case of 3-methylisoquinoline N-oxide, the chemical yield of lactam was also remained constant below ca.16kG, that is, 57% in ethanol and 43% in t-butyl alcohol.

Scheme



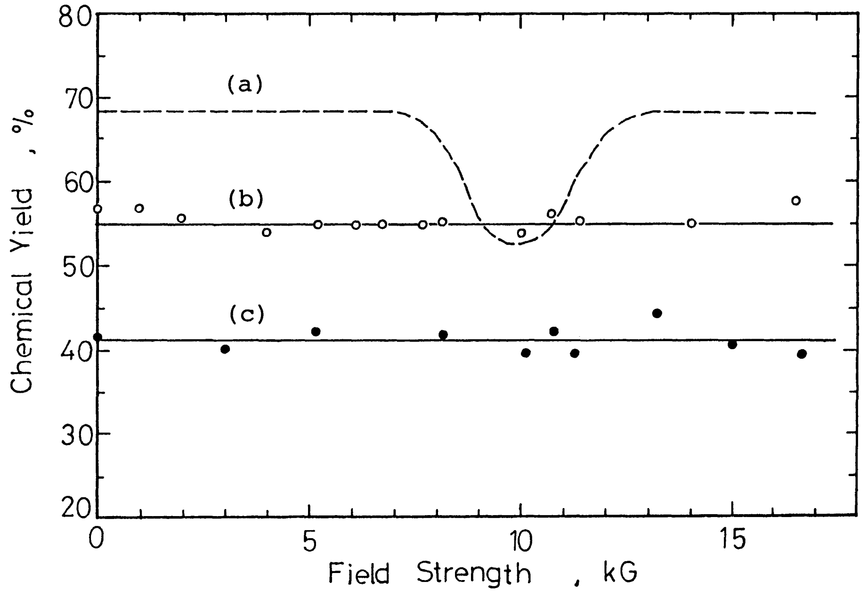


Figure Chemical yield of lactam vs magnetic field strength in the photochemical reaction of 4-bromoisoquinoline N-oxide. [N-Oxide] = 4.46 X 10^{-3}M and Conversion = ca.15%. Solvent: 50ml of ethanol ((b) —○—) and t-butyl alcohol ((c) —●—). Curve (a) shows the field dependence of the chemical yield of lactam in the photochemical reaction of isoquinoline N-oxide in ethanol.[2)]

The experimental results described above are well interpreted in terms of the radical ion pair mechanism as follows. Isoquinoline N-oxide molecule has two pairs of 2p non-bonding electron on the oxygen atom, one of which is in conjugation with the π-electron system of isoquinoline ring (πO:) and the other remains as non-bonding pair (σO:). It is also known that the photoelectron spectrum of this molecule shows the first band at 7.98eV to be due to the πO:,8) indicating that the N-oxide cation radical is a π-radical having a radical center on the oxygen atom of the N-O group. This is consistent with the assumption that the singlet radical ion pair 3 is a primary product from the S_1 state of isoquinoline N-oxide in hydroxylic solvents (cf. the Scheme), because hydrogen atom abstraction by the oxygen atom of the N-oxide cation radical from the ethanol anion radical within a solvent cage may occur to form the ion pair 4 responsible for Process I. The singlet radical ion pair 3 does also undergo magnetosensitive intersystem crossing (3 → 3') with rates of the order of 10^7-$10^8 s^{-1}$ via hyperfine interaction.9) Hence, only when the hydrogen atom abstraction (3 → 4) takes place in competition with the intersystem crossing (3 → 3'), Process I may be subject to magnetic field effect; in other words, if the former proceeds much faster than the latter, Process I may be insensitive to an external magnetic field. Meanwhile, π-electron migration from the oxygen atom of N-O group to the conjugated system of the isoquinoline ring is known to be depressed by substituting an electron-donating group for hydrogen of the ring, whereas it is facilitated by the substitution of an electron-withdrawing group.10) Therefore, the cation radical of isoquinoline N-oxide having an electron-donating substituent is supposed to have the increased odd π-electron density at the oxygen atom compared with the cation radical of unsubstituted isoquinoline N-oxide, and the radical character of the oxygen atom may be greatly enhanced. For this reason, the rate of hydrogen atom abstraction (3 → 4), by introducing an electron-donating substituent such as Br or CH_3 to the isoquinoline nucleus, becomes possibly much faster than the rate of intersystem crossing (3 → 3') to result in the disappearance of the magnetic field effect observed in the case of unsubstituted isoquinoline N-oxide (cf. the Figure). The results obtained in the present study is considered to provide strong evidence supporting the radical ion pair mechanism of Process I.

It is of interest to compare the present experimental results with the case of the photochemical isomerization of isoquinoline N-oxide bearing an electron-withdrawing group such as cyano or phenyl group, since such a substituent is expected to cause a significant decrease of the radical character of the oxygen atom of N-O group. However, unfortunately, 1-cyano- or phenyl-isoquinoline N-oxide does not undergo Process I, but Process II occurs from the S_1 state through the formation of oxaziridine intermediate to give rise to oxazepine1) (cf. the Scheme). It is because that the hydrogen bonding ability of N-oxide with a proton donor becomes vanishingly small by the introduction of an electron-withdrawing substituent.11)

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References

1) As a review, see, for example,
G.G.Spence, E.C.Taylor and O.Buchardt, Chem.Rev., 70, 231 (1970) and
F.Bellamy and J.Streith, Heterocycles, 4, 1391 (1976).

2) N.Hata, Chem.Lett., 1976, 547.

3) N.Hata, Chem.Lett., 1978, 1359.

4) The photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in ethanol was also found to show magnetic field effect due to HFI-J mechanism.[5)]

5) N.Hata and M.Hokawa, Chem.Lett., 1981, 507.

6) N.Hata, Y.Ono and F.Nakagawa, Chem.Lett., 1979, 603.

7) Cf. refs.2,3 and 6. The unreacted N-oxide and product (lactam) were separated by means of a thin layer chromatography (Merck TLC $60F_{254}$, layer thickness 2 mm; eluent, $CHCl_3$-ethyl acetate (1:3) in the case of 4-bromoisoquinoline N-oxide, and diethyl ether-$CHCl_3$ (2:1) in the case of 3-methylisoquinoline N-oxide). The amounts were determined spectrophotometrically.

8) J.P.Maier, J-.F.Muller, T.Kubota and M.Yamakawa, Helv.Chim.Acta, 58, 1641 (1975).

9) See, for example, N.J.Turro and B.Kraeutler, Acc.Chem.Res., 13, 369 (1980).

10) See, for example, E.Ochiai, "Aromatic Amine Oxides", Elsevier (1967), Chap.4.

11) We have revealed previously that hydrogen-bonding interaction between the N-oxide and solvent molecule (ROH) is essential for Process I, but not for Process II. Process II occurs with the formation of oxaziridine intermediate from the S_1 state. See N.Hata and I.Ono, Bull.Chem.Soc.Jpn., 49, 1794 (1976) and N.Hata and T.Oguro, Chem.Lett., 1978, 597.

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