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THE EFFECT OF EXTERNAL MAGNETIC FIELD ON THE PHOTOCHEMICAL REACTION OF ISOQUINOLINE N-OXIDE AND 2-CYANOQUINOLINE N-OXIDE

Norisuke HATA
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya, Tokyo 157

It was proved that in the photochemical reaction of quinoline N-oxides or isoquinoline N-oxides Process I (N-oxide → lactam) undergoes an external magnetic field effect, but Process II (N-oxide → oxazepine) does not. The magnetic field effect appears to be explained by assuming as the primary step of Process I the formation of an excited radical-ion pair.

It is well known that irradiations of quinoline N-oxide or isoquinoline N-oxide in solution result in the formation of lactam (Process I) and unstable oxazepine (Process II) from the lowest excited singlet state (cf. Scheme 1), but the deoxygenation product (the parent amine) originated from the lowest triplet state is obtained only in a few percent yield.1-3) It has been reported in a previous communication that when isoquinoline N-oxide in ethanol was irradiated in the presence of a magnetic field of 0-17 kG the chemical yield of lactam (isocarbostyril) showed a minimum at approximately 10 kG (curve (a) in Fig.1).4) The results have been tentatively assumed to be due to a magnetic perturbation for the intersystem crossing from the excited singlet state. However, this assumption appears extremely doubtful because no field dependence is observed upon the yield of deoxygenation product (isoquinoline) arising from the lowest triplet state. Thus, it may be rather reasonable to presume that Process I itself is subject to a magnetic perturbation, consequently the yield of lactam being reduced. In order to make this point clear, it is also necessary to elucidate whether or not Process II undergoes a magnetic field effect, although isoquinoline N-oxide is unsuitable as a sample for this purpose because the photoproduct "oxazepine" is too unstable to isolate. In the case of 2-cyanoquinoline N-oxide, only Process II occurs conveniently from the excited singlet state to give rise to the stable oxazepine in ca.90% yield.3,5) In the present study, therefore, the photochemical reaction of 2-cyanoquinoline N-oxide in benzene was examined in the absence and in the presence of a magnetic field (0-17 kG) and furthermore, we discussed the origin of the field dependence of the photochemical reaction of isoquinoline N-oxide.

The experimental procedure was quite similar to that described in a previous communication.4) In Fig.1, (b) and (c) show the results when the chemical yields of oxazepine and deoxygenation product (2-quinolinecarbonitrile) were plotted as a function of the field strength, from which the chemical yields were proved to be independent of a magnetic field. The results indicate clearly that neither Process II nor the intersystem crossing from the excited singlet state are influenced by a magnetic field.

It may safely be concluded from the above results that only Process I is sensitive to an external magnetic field. Thus, detailed examination of the mechanism of Process I would be required to elucidate the origin of such a magnetic field effect. We have recently demonstrated[1-3] that in the photochemical reaction of quinoline N-oxides or isoquinoline N-oxides (i) a hydrogen-bond formation between the N-oxide oxygen atom and a solvent molecule is essential for Process I, but not for Process II, and (ii) Process I proceeds via an excited ion pair resulting from a protonation of the N→O group through a hydrogen bonding interaction in the excited singlet state, whereas Process II occurs with the formation of an oxaziridine intermediate from the excited singlet state, as shown in Scheme 1. In the case of pyridine N-oxide, however, there occur a variety of photochemical reactions (mostly decomposition and polymerization) arising from the oxaziridine intermediate, but appreciable amounts of the lactam (2-pyridone) are not produced even in a hydroxylic solvent.[6] This means that a hydrogen bonding interaction between the N-oxide oxygen atom and a solvent molecule is a necessary but not sufficient condition for Process I. Also, it has been reported that the ionization energy of pyridine N-oxide (8.38 eV)[7] is greater than that of quinoline N-oxide (8.00 eV)[8] or isoquinoline N-oxide (7.98 eV)[8] and the pK_a values of these N-oxides are smaller in the excited singlet state than in the ground state.[9] These facts suggest that the formation of excited ion pair in Process I is not due to a direct protonation of the N→O group but rather due to an electron transfer followed by a hydrogen transfer between the excited singlet N-oxide and a solvent molecule (ROH) as shown in Scheme 2.

The above consideration leads to the conclusion that when quinoline N-oxide or isoquinoline N-oxide is irradiated in a hydroxylic solvent both an electron transfer from the excited singlet N-oxide to ROH (thus the formation of an excited radical-ion pair) and a conversion of the excited N-oxide to an oxaziridine intermediate take place as the primary photochemical act (Scheme 2). Since the excited radical-ion pair thus formed is in an overall singlet spin state (S), the components of the pair do not diffuse apart, but there may occur a hydrogen transfer between the two components to form an excited ion pair responsible for Process I. Assuming that the transition of this radical-ion pair to the triplet spin state (T) results finally in a deactivation to the ground state (Scheme 2), the magnetic field effect upon the photochemical reaction of isoquinoline N-oxide in ethanol can be interpreted qualitatively as follows.

As is well-known, a mixing between the singlet (S) and triplet (T) levels of a radical-ion pair can be induced by a hyperfine interaction of the unpaired electron with the nuclei in each component of the pair, provided the exchange interaction in this pair is negligible.[10] In the present case, however, the exchange interaction (J) is not neglected (that is, the S and T levels are non-degenerate, having an energy of 2J) because the excited radical-ion pair exists as a hydrogen bonding system,[11] and so the singlet-triplet mixing due to a hyperfine interaction could not occur in zero field. Application of a magnetic field to this system can resolve the triplet (T) into T_0, T_{+1} and T_{-1} levels. The T_{+1} level approaches the S level with an increase in the field strength and consequently the S-T_{+1} mixing may occur at field strengths in which the S-T_{+1} energy gap is of the order of the hyperfine interactions. The S-T_{+1} mixing is largest at a given magnetic field in which the S and T_{+1} levels lie at the same energy. Further increase in the field strength results in an increase of the separation between the levels of S and T_{+1} so that the extent of $S-T_{+1}$ mixing decrease rapidly. Therefore, it would easily be understandable that the chemical yield of lactam shows a minimum at the magnetic field of about 10 kG in which the $S-T_{+1}$ mixing is probably most favorable.

A magnetic perturbation which induces such a singlet-triplet mixing can also arise from the difference (Δg) in the g-value of the radical-ions[10]; the Δg interaction, which is inoperative at the zero field, is caused by an external magnetic field to prompt the $S-T_0$ transition at a rate which increases with the strength of the applied field. In such a case the chemical yield of lactam is expected to decrease monotonically with increasing strength of the magnetic field, although the observed field dependence (curve (a) in Fig.1) is quite different from the expectation; thus the Δg mechanism can be ruled out.

Meanwhile, Kaneko and Buchardt have independently postulated that an oxaziridine may be initially formed as a photochemical intermediate common to both Processes I and II.[5,12] According to this mechanism, Process I as well as Process II should be independent of an external magnetic field. In the present investigation, however, only Process I was found to show the magnetic field dependence. This supports strongly the author's view that Process II involves an oxaziridine intermediate, but Process I does not.[1-3]

Further studies are now in progress. The author wishes to thank Professor Saburo Nagakura of the University of Tokyo for his valuable discussion and Miss Keiko Ohshima for her technical assistance.

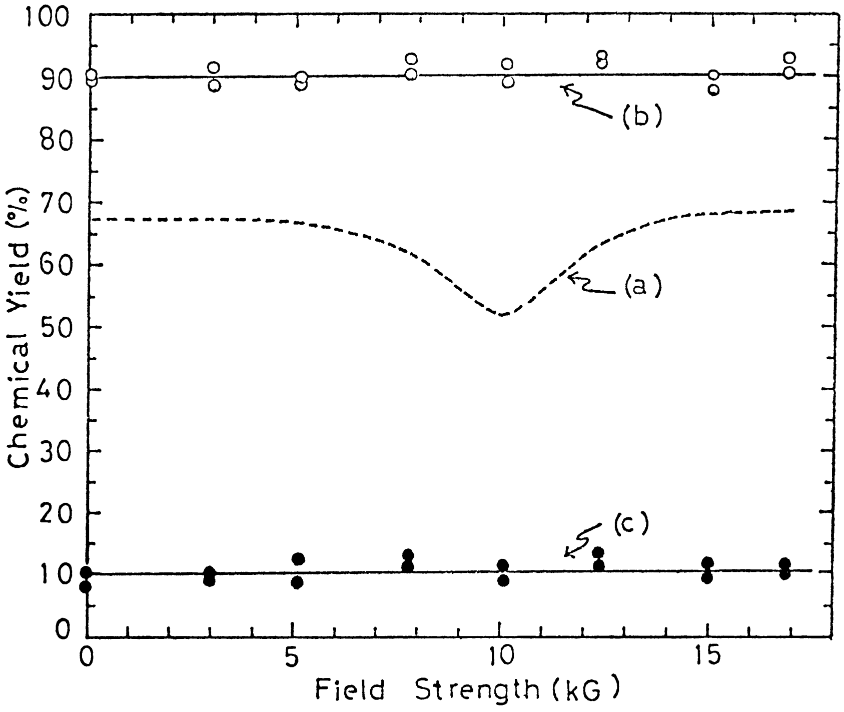
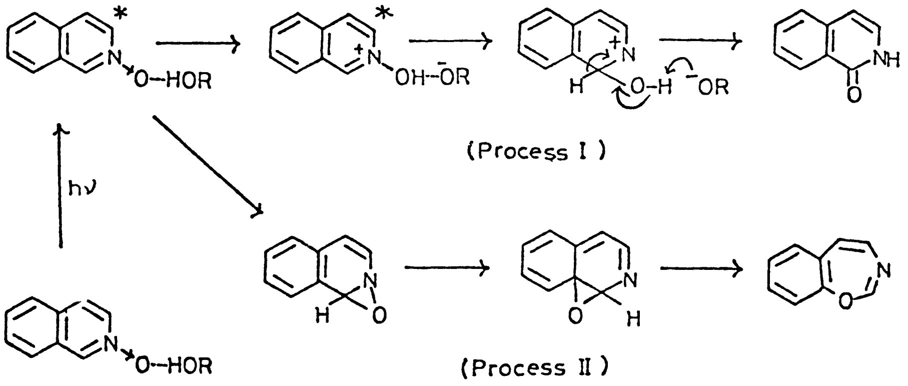
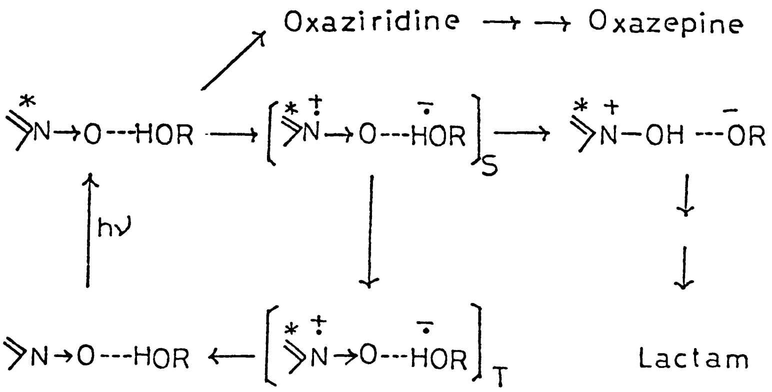


Fig.1 The Effect of External Magnetic Field on the Photochemical Reaction of 2-Cyanoquinoline N-Oxide. [N-Oxide]: 5.29×10^{-3} M, solvent: 50 ml of benzene, and conversion: ca.20%. (b) —○— : chemical yield of the oxazepine and (c) —●— : chemical yield of the deoxygenation product. Curve (a) shows the field dependence of the chemical yield of lactam in the photochemical reaction of isoquinoline N-oxide in ethanol.[4]

Scheme 1



Scheme 2



References and Notes

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11) The hydrogen bonding interaction of aromatic amine N-oxide molecules with a proton donor is weaken in the excited singlet state than in the ground state. See, for example, N.Mataga and T.Kubota, "Molecular Interactions and Electronic Spectra", M.Dekker (1970), Chapter 7.

12) Cf. literatures cited in Ref.1.

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