CHEMISTRY LETTERS, pp. 603-606, 1979. Published by the Chemical Society of Japan

THE EFFECT OF EXTERNAL MAGNETIC FIELD ON THE PHOTOCHEMICAL REACTION OF ISOQUINOLINE N-OXIDE IN VARIOUS ALCOHOLS

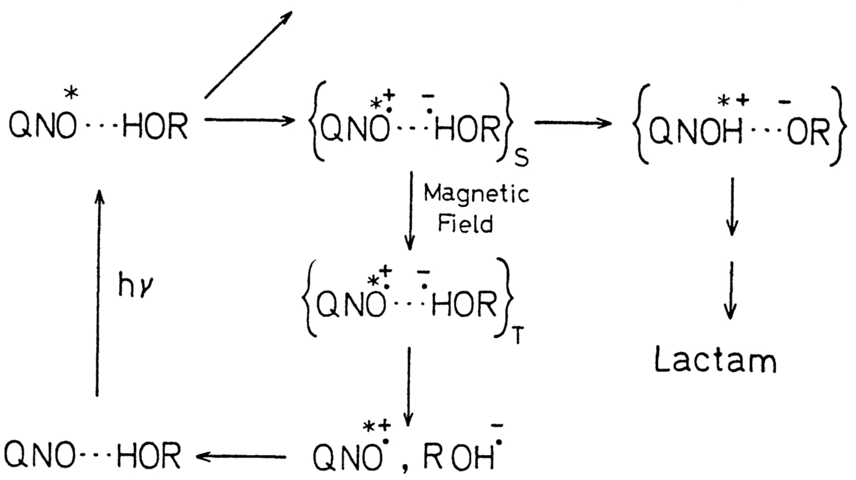
Norisuke HATA,* Yumiko ONO, and Fumiaki NAKAGAWA
Department of Chemistry, College of Science and Engineering,
Aoyama Gakuin University, Chitosedai, Setagaya, Tokyo 157

The external magnetic field effect on the photochemical reaction of isoquinoline N-oxide was studied in methanol, 2-propanol or tert-butyl alcohol. Consequently, the yield of lactam was found to show a minimum at higher fields with a decrease in the pK_a value of alcohol used as a solvent, supporting the previously proposed mechanism of the photochemical magnetic field effect.

Quinoline N-oxides or isoquinoline N-oxides in hydroxylic solvents undergo the two types of photochemical reactions arising from the excited singlet state:[1)] (i) photorearrangement to the lactam via the formation of an excited ion pair through a hydrogen bonding interaction between the N-oxide oxygen atom and solvent molecule (Process I), and (ii) photoisomerization to the oxazepine via an oxaziridine intermediate (Process II). As shown in Scheme 1, the formation of an excited ion pair in Process I is reasonably assumed not to be due to a direct protonation of the $N \rightarrow O$ group but due to an electron transfer followed by a hydrogen transfer between the excited singlet N-oxide and solvent molecule.[2)] Since the excited radical-ion pair thus formed is in an overall singlet spin state (S), the components of the pair do not escape from the solvent cage, but a hydrogen transfer between them takes place to form an excited ion pair responsible for Process I. The transition from the initially formed singlet (S) to a triplet pair state (T) results in the separation of components by diffusion, and the free radical-ions diffused into the solvent bulk encounter members of other pairs and recombine. However, the singlet-triplet transition is not considered to occur in the absence of a magnetic field because the exchange interaction in such a pair is greater than the hyperfine energies owing to the hydrogen bonding system.

It has been reported in previous communications[2,3)] that in the photochemical reaction of isoquinoline N-oxide or 2-cyanoquinoline N-oxide Process I (N-oxide → lactam) was sensitive to an external magnetic field, but Process II (N-oxide → oxazepine) did not; in the case of an ethanol solution of isoquinoline N-oxide, interestingly, the chemical yield of lactam was found to show a minimum at approximately 10 kG (curve (a) in Fig.2).[3)] This has been qualitatively well interpreted, based on the reaction mechanism shown in Scheme 1, to be due to a crossing of the levels of S and T_{+1}, whereupon a mixing between the two levels due to a hyperfine interaction is largest, in the intermediate radical-ion pair (Fig.1).[2)] If the interpretation is valid, the magnetic field responsible for the minimal yield of

Scheme 1



QNO = Isoquinoline N-Oxide or Quinoline N-Oxide

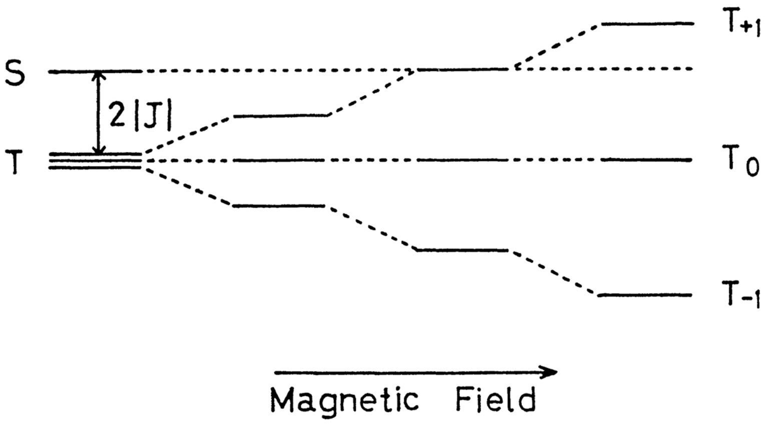


Fig.1 Energy diagram of the singlet and triplet pair state for an external magnetic field.

lactam is expected to be progressively shifted to higher fields with a decrease in the pK_a of ROH used as a solvent, because the exchange interaction (J) depends on the distance between the components of the pair so that it may become greater as the pK_a value of ROH is decreased. As is well known, the pK_a value of simple aliphatic alcohol is in the following order:4) methanol < ethanol ≈ 2-propanol < tert-butyl alcohol. In the present investigation, therefore, the photochemical reaction of isoquinoline N-oxide in methanol, 2-propanol or tert-butyl alcohol was examined in the absence and in the presence of a magnetic field (0-16 kG).

The experimental procedure was quite similar to that described in a previous communications.3) Figure 2 shows the result when the chemical yield of lactam was plotted as a function of the field strength. In the case of a 2-propanol solution (curve (b)), the yield of lactam showed a minimum at about 10 kG, just as in the case of an ethanol solution (curve (a)).3) In the case of tert-butyl alcohol solution (curve (c)), however, the minimal yield was observed at the magnetic field of approximately 7 kG. When methanol was used as a solvent (curve (d)) the yield of lactam remained constant at magnetic fields below 12 kG, but it decreased with an increase in the field strength; a minimum in the yield seems to be in the 17 to 18 kG region.5)

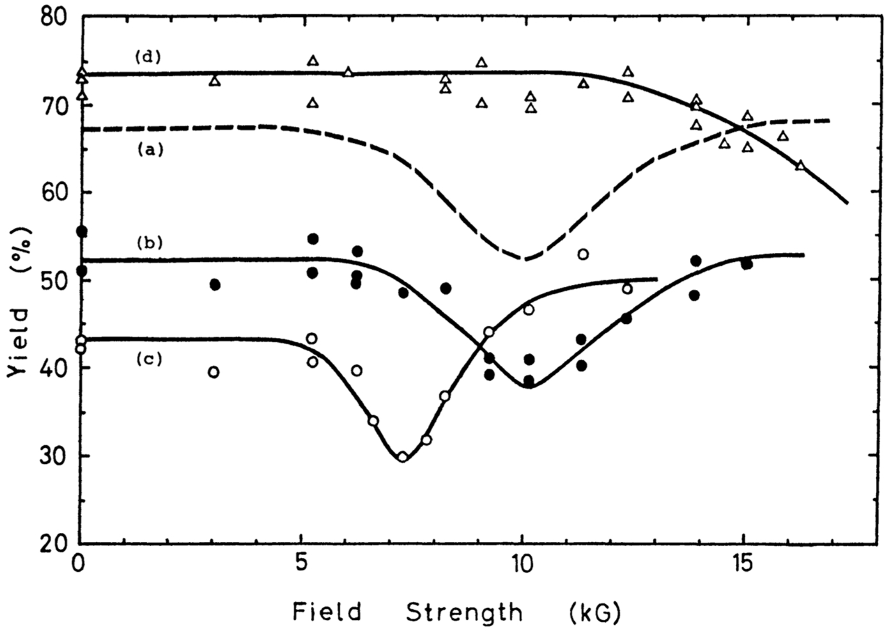


Fig.2 Chemical yield of lactam as a function of field strength.
[N-Oxide] = 7.40×10^{-3}M and Conversion = ca.15%.
Solvent : 50 ml of ethanol ((a) ---),3) 2-propanol ((b) —●—), tert-butyl alcohol ((c) —○—) and methanol ((d) —△—).

It may safely be concluded from the experimental result described above that when isoquinoline N-oxide is irradiated in alcoholic solvents in the presence of a magnetic field the yield of lactam shows a minimum at a given magnetic field which is, in accord with the expectation, progressively shifted to higher fields with a decrease in the pK_a value of solvent. This supports strongly the interpretation of the photochemical magnetic field effect to be due to a level-crossing in the intermediate radical-ion pair formed in the primary step of Process I.[2] However, it should be noted that in the case of a tert-butyl alcohol solution (curve (c)) the yield of lactam at higher fields (> 10 kG) is greater than that at lower fields (< 5 kG), although the origin is still ambiguous at present.

Further studies are now in progress.

References and Notes

1) N.Hata and I.Ono, Bull.Chem.Soc.Jpn., 49, 1794 (1976).
   N.Hata and T.Oguro, Chem.Lett., 597 (1978).
   For a recent review on the photochemistry of aromatic amine N-oxides, see F.Bellamy and J.Streith, Heterocycles, 4, 1391 (1976).
2) N.Hata, Chem.Lett., 1359 (1978).
3) N.Hata, Chem.Lett., 547 (1976).
4) W.K.McEwen, J.Am.Chem.Soc., 58, 1124 (1936).
5) The photochemical reaction was not investigated in magnetic fields higher than 17 kG because of the limited capability of the electromagnet employed here.

(Received March 12, 1979)