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THE EFFECT OF EXTERNAL MAGNETIC FIELD ON THE PHOTOINDUCED SUBSTITUTION REACTION OF 4-METHYLQUINOLINE-2-CARBONITRILE IN ETHANOL

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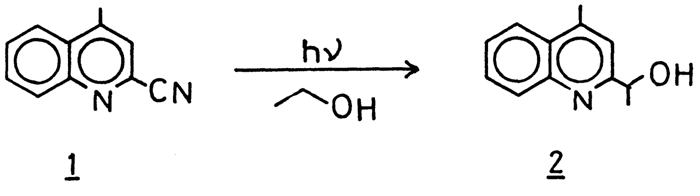
The photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in ethanol was found to undergo external magnetic field effect due to both HFI-J and Δg mechanisms. The present study is also considered to provide definitive evidence that the reaction proceeds primarily through hydrogen abstraction by the ring nitrogen from the hydrogen-bonded ethanol in the S_1 state.

External magnetic field effect can be expected for chemical reactions involving a radical pair intermediate because an external field influences the rate of the singlet-triplet transition of radical pair in a solvent cage.1) In case that the component radicals separate to a distance where the exchange interaction (J) is disregarded, the magnetic field effect is explained in terms of the following mechanisms: (i) magnetic enhancement of the rate of singlet-triplet transition in a radical pair by virtue of the different g-values of component radicals (Δg mechanism) and (ii) magnetic field perturbation of the hyperfine-induced singlet-triplet transition in a radical pair (HFI mechanism).

We have found previously that when isoquinoline N-oxide in ethanol was irradiated in the presence of a magnetic field the chemical yield of lactam (isocarbostyril) produced showed a minimum at approximately 10 kG.2) In order to interpret the new phenomenon, we proposed a hyperfine interaction mechanism including the exchange interaction in radical pair intermediate3); hereafter, it will be referred to as HFI-J mechanism. The observation of such a field dependence of the chemical yield was also considered unambiguous evidence supporting a mechanism that the photoisomerization of N-oxide to lactam proceeds via a singlet hydrogen-bonded radical-ion pair but not an oxaziridine intermediate responsible for the photoisomerization to oxazepine. In order to find another example of this type of photochemical magnetic field effect, the present authors examined the photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile 1 in ethanol (Eq.1)4) in the presence and absence of an applied magnetic field (0-17 kG), for the reaction is assumed to



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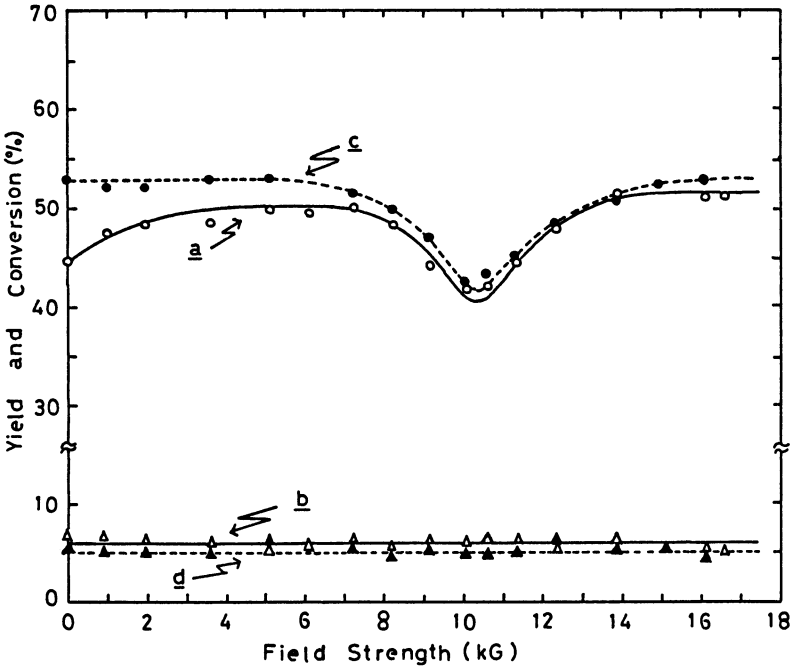
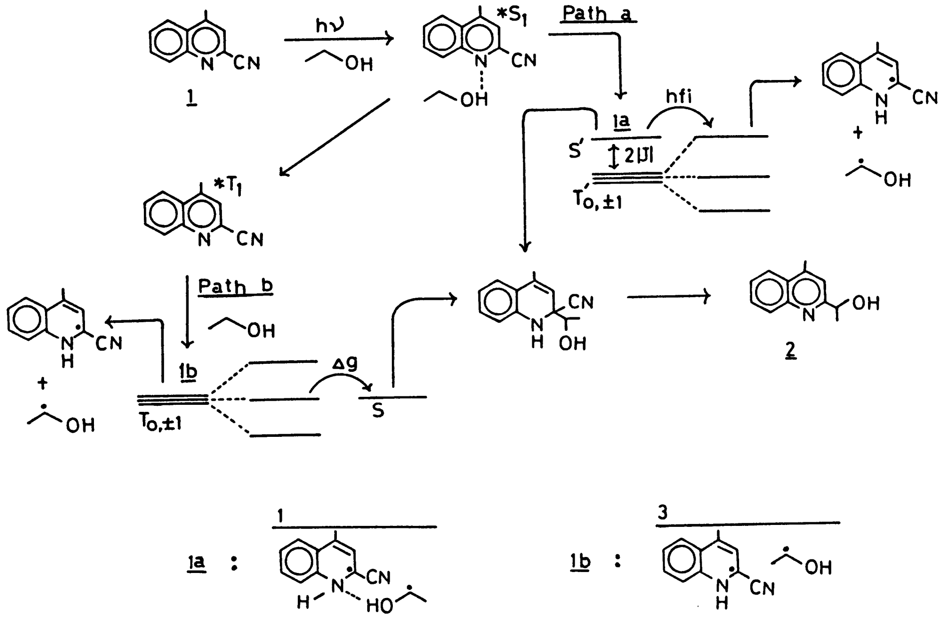


Fig.1 Chemical yield of 2 and conversion as a function of magnetic field strength. [N-Oxide]=4.76×10^{-3}M, Solvent: 50 ml of ethanol. a and b (——): yield of 2 (○) and conversion (△), [Piperylene]=0.
c and d (---): yield of 2 (●) and conversion (▲), [Piperylene]=3.0×10^{-1}M.

Scheme 1



involve a singlet hydrogen-bonded radical pair 1a (Scheme 1)$^{5)}$ in which the exchange interaction is greater than the hyperfine energy.

The experimental procedure was the same as reported previously$^{6)}$; a 50 ml of ethanol solution containing 40 mg of 1 (4.76×10^{-3}M) in a quartz vessel was placed in an electromagnet and was irradiated with a 500W Ushio high-pressure mercury lamp (USH-500D) equipped with a Toshiba filter UV-31 for 3h in nitrogen atmosphere. The unreacted nitrile 1 and product 2 (2-(1-hydroxyethyl)-4-methylquinoline) were separated by means of a thin layer chromatography (Merck TLC silicagel plate 60 F_{254}, layer thickness 2 mm; eluent, a mixture of n-hexane and ethyl acetate (5:1)) and the amounts were determined spectrophotometrically.

Full curves a and b in Fig.1 show, respectively, the plots of the chemical yield of 2 and conversion against magnetic field strength. The yield of 2 was ca.45% at zero field (earth's magnetic field), but it increased quadratically as field strength increased, i.e., the magnetic field effect due to Δg mechanism. Furthermore, the chemical yield showed a minimum at about 10 kG, i.e., the magnetic field effect due to HFI-J mechanism. The conversion remained almost unchanged.

First we discuss the magnetic field effect due to HFI-J mechanism observed in the region of about 6 to 15 kG. The photosubstitution reaction of 2-quinolinecarbonitriles in ethanol has been reported to proceed via the S_1 state$^{7)}$ through hydrogen abstraction by the ring nitrogen from the hydrogen-bonded ethanol (Path a in Scheme 1), where the singlet radical pair intermediate 1a which undergoes cage recombination responsible for the formation of 2 was assumed to exist as a hydrogen bonding system.$^{5)}$ If this is true, the exchange interaction in the pair is not disregarded, but it should be large relative to the electron-nuclear hyperfine energy because the radical centers are in close proximity owing to the hydrogen bonding interaction. Therefore, the singlet(S')-triplet(T') mixing due to hyperfine interaction does not occur in zero field (Scheme 1). As shown in Scheme 1, however, application of a magnetic field to this system can resolve the triplet into T'_0, T'_{+1} and T'_{-1} levels so that the S'-T'_{+1} mixing due to hyperfine interaction (hfi) occurs in the region of magnetic fields where Zeeman splitting of the triplet level is comparable to S'-T' separation ($2|J|$). The efficiency of S'-T'_{+1} transition passes through a maximum at the magnetic field where the S' level is in resonance with T'_{+1} level, and the chemical yield of 2 as a cage product shows a minimum at this field strength (ca.10 kG). Thus the observed magnetic field effect is well explained in terms of HFI-J mechanism, just as in the case of the photoisomerization of isoquinoline N-oxide to lactam.$^{3)}$ Alternatively the present data may be considered strong evidence for the reaction mechanism postulated the intervention of a singlet hydrogen-bonded radical pair intermediate 1a which originates from hydrogen abstraction by the ring nitrogen from the hydrogen-bonded ethanol in the S_1 state.

On the other hand, the observation of a magnetic field effect due to Δg mechanism suggests strongly that there occurs hydrogen abstraction by the ring nitrogen from an ethanol in the T_1 state$^{7)}$ (Path b in Scheme 1). The resulting radical pair 1b is in a triplet spin state so that the components diffuse from the solvent cage into the solvent bulk. The escaped radicals may partly recombine as a result of a random encounter to give rise to 2, but largely react with the solvent molecule. The fact that the chemical yield of 2 increases quadratically with increasing field strength indicates definitely the occurence of the Δg interaction causing a transition from the triplet (T_0) to singlet (S) in radical pair 1b (Scheme 1), just as in the case of the photosubstitution of 1-isoquinolinecarbonitrile6); the singlet radical pair thus formed undergoes efficient recombination to generate 2. If the interpretation is valid, the magnetic field effect due to Δg mechanism would have to disappear by the addition of piperylene (triplet quencher).8) Therefore, we examined the field dependence of the chemical yield of 2 and conversion in the presence of piperylene (3.0×10^{-1}M). Consequently, as shown in Fig.1 (dashed curves c and d), the magnetic field effect due to Δg mechanism disappeared completely, but the magnetic field effect due to HFI-J mechanism did not. The conversion was almost independent of an applied magnetic field. The results demonstrate that hydrogen abstraction by the ring nitrogen occurs in the T_1 state to generate the triplet radical pair 1b which is subject to Δg interactions.

In summary, the photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in ethanol was found to undergo magnetic field effect due to both HFI-J and Δg mechanisms. It was deduced from the experimental results that the reaction proceeds by a mechanism in Scheme 1 and that the singlet hydrogen-bonded radical pair 1a is responsible for the magnetic field effect due to HFI-J mechanism, whereas the triplet radical pair 1b is concerned in the magnetic field effect due to Δg mechanism.

References and Notes

1) See, for example,
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5) a) N.Hata and T.Saito, Bull.Chem.Soc.Jpn., 47, 942 (1974).
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   c) N.Hata and R.Ohtsuka, Chem.Lett., 1975, 1107.
6) N.Hata and Y.Yamada, Chem.Lett., 1980, 989.
7) It is concluded from the solvent effects on the absorption, fluorescence and phosphorescence spectra of quinoline-2-carbonitriles that the ring nitrogen forms a hydrogen bond with ethanol in the S_1 state, but such a hydrogen bond does not exist in the S_0 and T_1 states.5a,5c)
8) The excitation energy of the T_1 state of 1 is estimated, from the first maximum (486 nm) of the phosphorescence in ethanol, to be 58.8 kcal.mol^{-1}, and piperylene is usable as a triplet quencher for 1.5c)

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