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

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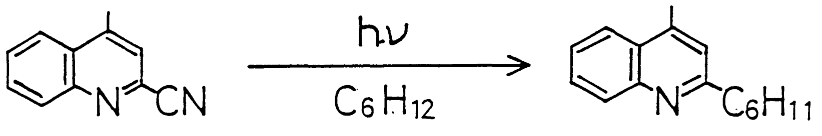
The photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in cyclohexane was found to show an external magnetic field effect due to HFI and Δg mechanism. It was revealed that (i) the photoreaction occurs from the S_1 state as well as T_1 states and (ii) the triplet radical pair intermediate 2b is responsible for the observed magnetic field effect, whereas the singlet radical pair intermediate 2a is insensitive to an external magnetic field.

About seven years ago a magnetic field effect due to HFI-J mechanism (level-crossing mechanism) has been found for the first time by one of the authors (N.H.) in the photoisomerization of isoquinoline N-oxide in ethanol, the chemical yield of product (lactam) being observed to show a minimum at about 1 T.[1,2] As a result of this finding, the photochemical isomerization was disclosed to proceed with the intervention of a singlet hydrogen-bonded radical ion pair, but it does not involve an oxazepine intermediate postulated before.[3,4]

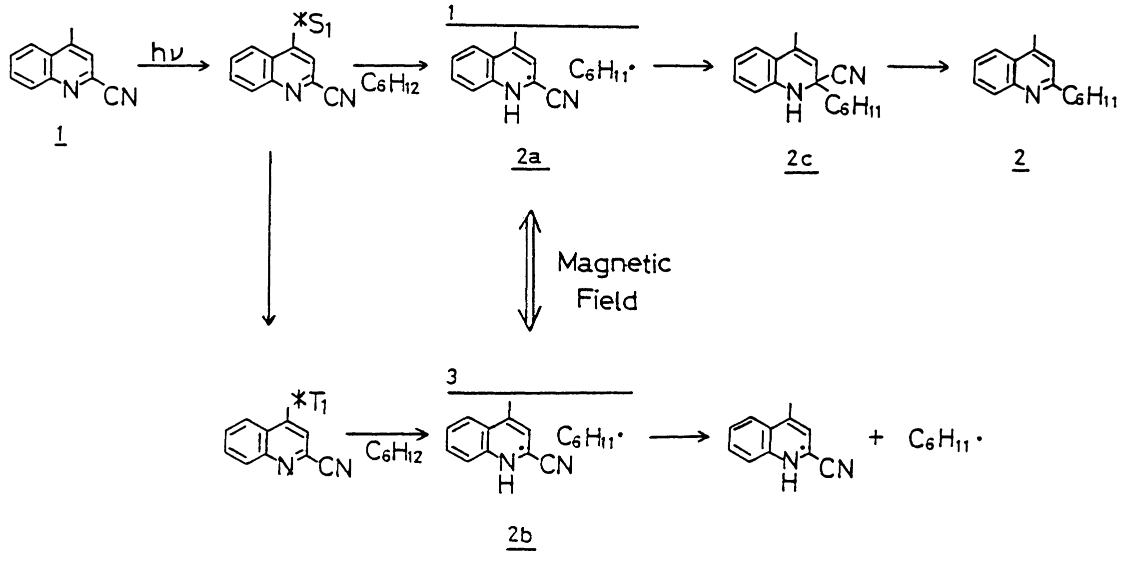
Later the second example of this type of magnetic field effect has been found in the photosubstitution reaction of 4-methylquinoline-2-carbonitrile in ethanol,[5] providing conclusive proof that the reaction occurs from the S_1 state through the formation of singlet hydrogen-bonded radical pair. A similar photoinduced substitution reaction occurred in a cyclohexane solution; irradiations of 4-methylquinoline-2-carbonitrile 1 in cyclohexane under a nitrogen atmosphere resulted in the replacement of the cyano group at the 2-position of a quinoline nucleus by the cyclohexyl group to give 2-cyclohexyl-4-methylquinoline 2 in ca.65% yield.[6]



1 2

The reaction is also assumed to be initiated by hydrogen abstraction from the solvent molecule by the ring nitrogen in the S_1 state (Scheme 1). Differring from the case of the photoreaction in an ethanol solution, however, the singlet radical pair 2a thus formed is not a hydrogen bonding pair of radicals in close

Scheme 1



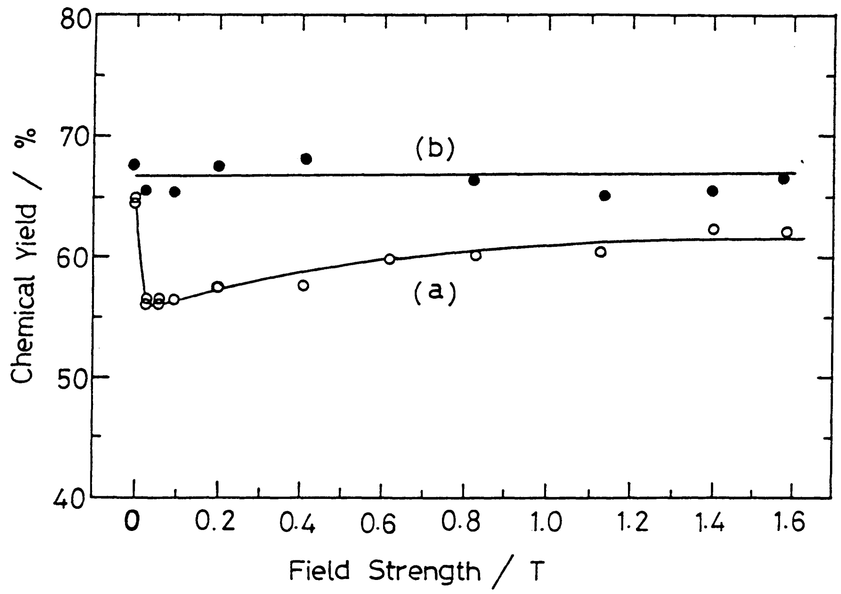


Fig.1. Chemical yield of 2 vs. magnetic field strength.
[1] = 3.80×10^{-3} mol dm^{-3} and Conversion = ca.20%
Solvent: 50 ml of cyclohexane.
(a) —○— : chemical yield of 2 in the absence of piperylene
(b) —●— : chemical yield of 2 in the presence of piperylene (3.0×10^{-1} mol dm^{-3})

proximity. Therefore, the exchange interaction between the two unpaired electrons may be disregarded. If it is the case, a magnetic field effect due to HFI-J mechanism could not be expected for this reaction. In order to confirm this, we examined the effect of external magnetic field on the photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in cyclohexane.

The experimental procedure was quite similar to that described in a previous communication.[7)] The results are shown in Fig.1. As can be seen from curve (a) in the figure, the chemical yield of 2 was ca.65% at zero field (earth's magnetic field), but it decreased steeply by application of a magnetic field of 30-80 mT to be ca.56%. Further increase in the field strength resulted in a quadratic increase in the yield to approach ca.62% at approximately 1.6 T. As shown by solid line (b) in the figure, however, such a magnetic field effect disappeared completely by the addition of piperylene as a triplet quencher. The conversion remained almost constant (ca.20%) in either case.

The experimental results described above are summarized below, which can be explained in terms of a reaction mechanism as shown in Scheme 1: (i) The photoinduced substitution reaction of 4-methylquinoline-2-carbonitrile in cyclohexane occurs from both the S_1 and T_1 states through the formation of radical pairs 2a and 2b; the chemical yields of the S_1- and T_1-derived products 2 are estimated to be approximately 51.5 and 13.5%, respectively.[8)] (ii) The triplet radical pair 2b is responsible for the observed magnetic field effect (HFI and Δg mechanisms), whereas the singlet radical pair 2a is insensitive to an external magnetic field.

The observation of a magnetic field effect, as shown by curve (a) in Fig.1, in the absence of piperylene indicates clearly that the reaction occurs in part from the T_1 state; hydrogen abstraction by the ring nitrogen from a cyclohexane takes place in the T_1 state to form the triplet radical pair 2b which undergoes intersystem crossing to the singlet radical pair 2a via hyperfine interaction, leading to the formation of cage product 2. Application of a magnetic field to this system results in a reduction of the number of effective working channels for the hyperfine-induced intersystem crossing of the radical pair. Consequently, the chemical yield of cage product 2 decreases greatly at very low fields (magnetic field effect due to HFI mechanism). External magnetic field also causes Δg interaction in the triplet radical pair 2b to result in the intersystem crossing, and the chemical yield of 2 increases quadratically with the strength of the applied field (magnetic field effect due to Δg mechanism).

However, the triplet reaction pathway mentioned above is not considered to be a main path for the photosubstitution reaction in a cyclohexane solution. That the chemical yield of 2 amounts to ca.66% in the presence of piperylene (Fig.1) suggests strongly the photoreaction ($1 \rightarrow 2$) to proceed primarily via the S_1 state through the formation of singlet radical pair 2a. The singlet reaction was also shown not to be subject to magnetic field effect due to HFI-J mechanism (solid line (b) in Fig.1), which is consistent with the fact that 2a is not a hydrogen bonding pair. Interesting was that the singlet reaction different from the triplet one did not show even a magnetic field effect due to HFI or Δg mechanism. This may be interpreted as follows. As shown in Scheme 1, the singlet radical pair 2a undergoes two processes, one of which is a cage recombination of the component radicals (2a → 2c) and the other a magnetosensitive intersystem crossing (2a → 2b) whcih occurs with rates of the order of 10^7-10^8 s^{-1} via hyperfine interaction.[9] The singlet radical pair 2a is supposed to be subject to magnetic field effect provided the cage recombination takes place in competition with the intersystem crossing. Therefore, the fact that the singlet reaction is field-independent probably means the cage recombination to be much faster than the magnetosensitive intersystem crossing. Similar interpretation has been made on the magnetic field effect upon the photochemical isomerization of 4-bromoisoquinoline N-oxide in hydroxylic solvents.[4]

References

1) N.Hata, Chem.Lett., 1976, 547.
2) N.Hata, Chem.Lett., 1978, 1359.
3) N.Hata, Y.Ono and F.Nakagawa, Chem.Lett., 1979, 603.
4) N.Hata and A.Yagi, Chem.Lett., 1983, 309.
5) N.Hata and M.Hokawa, Chem.Lett., 1981, 507.
6) Details of this and related reactions will be reported elsewhere.
7) Cf. Ref.5. The unreacted nitrile 1 and product 2 were separated by means of a thin layer chromatography (Merck TLC $60F_{254}$, layer thickness 2 mm; eluent, n-hexane – ethyl acetate (5:1)). The amounts were determined spectrophotometrically.
8) These values are estimated from the data in Fig.1(a) in the following way. The sum of the chemical yields (Y_S and Y_T) of product 2 derived from the S_1 and T_1 states is equal to the chemical yield ($Y° = 65\%$) at zero field; $Y° = Y_S + Y_T$. The chemical yield ($Y^H = 56\%$) at 30 mT is given as follows, assuming the chemical yield of T_1-derived product 2 to be $(1/3)Y_T$ because of the HFI effect: $Y^H = Y_S + (1/3)Y_T$. Thus, Y_S and Y_T are evaluated from the above two equations to be about 51.5 and 13.5%, respectively.
9) See, for example, N.J.Turro and B.Kraeutler, Acc.Chem.Res., 13, 369 (1980).

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