CIDNP Studies on the Photochemical Reaction of 4-Methyl-2-quinolinecarbonitrile with Optically Active (*S*)- or (*R*)-2-Phenylpropionic Acid. No Evidence for the Chiral Symmetry Breaking

Sameh Saad Ali, Kiminori Maeda, and Tohru Azumi*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980-77

(Received December 5, 1994)

The photochemical reactions of 4-methyl-2-quinolinecarbonitrile (MQCN) with the enantiomers of 2-phenylpropionic acid (PPA) has been studied by CIDNP technique. The problem of chemical behavior discrimination of the enantiomers of PPA proposed by Hata[1] was examined. In contrast to the proposal of Hata, both (R) and (S) forms of PPA are shown to have radical intermediates in their reaction with MQCN.

Hata[1] reported an example of chemical behavior discrimination between the enantiomers of 2-phenylpropionic acid (PPA) in the photochemical reaction with 4-methyl-2-quinolinecarbonitrile (MQCN) to yield 2-(1-phenylethyl)-4-methylquinoline (PEMQ). He claimed that the magnetic field dependence of the product yields and the optical activity of the product PEMQ observed for the reaction of MQCN with the two enantiomers of PPA are different. The essential conclusion proposed in his work was that the (S) reaction occurs with the formation of an ion-pair intermediate whereas (R) reaction involves a radical-pair intermediate.

Since the proposed difference in the chemical reactivity between the two enantiomers is in conflict with the general understanding, it is important that some experimental efforts be devoted to reexamine the proposed mechanism. Since CIDNP phenomenon arises only when radical pairs are involved in the chemical reaction, it is an ideal technique to discriminate between the radical mechanism and the ion-pair mechanism. That is, if Hata's proposal is correct, CIDNP would be observed only in the reaction with the (R) form. The present work aims mainly to explore the proposed difference in the chemical behavior of the mentioned enantiomers using the CIDNP technique.

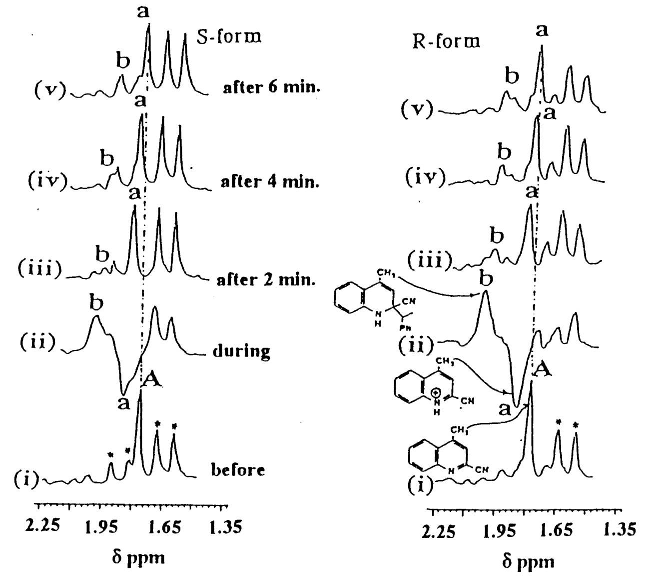
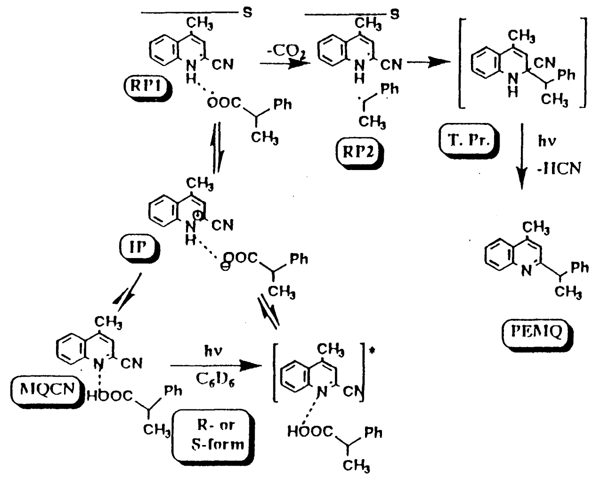


Figure 1. ^{1}H-CIDNP spectra recorded during the photochemical reactions of MQCN with (R) form (to the right) and (S) form (to the left) of PPA. Asterisk (*) stands for the spinning side bands.

CIDNP effect is observed in the region of the methyl group of MQCN. Figure 1 presents the part of the ^{1}H-NMR spectra (δ=1.35-2.25 ppm) containing the peak of the methyl group. Spectra (iii)-(v) are the NMR spectra recorded at 2, 4 and 6 minutes after cutting the irradiation light off.

In spectrum (ii) two CIDNP signals are observed. One is the emissive CIDNP at δ=1.85 ppm (peak a) and the other is the enhanced absorptive CIDNP at δ=2.05 ppm (peak b). None of these CIDNP peaks exists in the spectrum of either the reactant MQCN (spectrum (i)) or the product (spectrum (v)). Spectra (iii-v) show that the CIDNP peak (peak a) converges to the position of the methyl group of MQCN (peak A at δ=1.80 ppm) which is absent in spectra (ii-iv). The observed peak shift (i.e. difference between peaks A and a) persists for about 6 minutes after cutting the light off (the same behavior is observed for peak b). Before making the assignment, however, we wish to emphasize that (R)- and (S)-PPA show similar CIDNP in their reaction with MQCN. This means that *both (R) and (S) forms of PPA react through radical pair intermediates*. It is important to note that this conclusion is independent of the assignment of the CIDNP peaks, for which we attempt to make in the following.



Scheme 1. Proposed mechanism of the photochemical reaction of MQCN with (R)- or (S)-2-phenylpropionic acid.

In order to interpret the above experimental observations, we propose the reaction mechanism shown in Scheme 1.

The observed CIDNP features are interpreted in terms of the proposed reaction scheme as follows: First of all, we assign the CIDNP as due to the methyl group(s) of the species IP in scheme 1 (in equilibrium with the parent MQCN) formed from RP1 by electron transfer recombination reaction; c.f. scheme 1. The emissive polarization arises in the singlet RP1 due to an S-T_+ mixing process which requires a large exchange integral (J).[2] The large J value may arise due to hydrogen bonding in the intermediate RP1. To account for the observed δ value shift, we suggest that a fast exchange between the NMR peaks corresponding to the cationic and the parent MQCN leads to the appearance of a resultant band. The position of the resultant peak should be sensitive to the relative proportions of the two contributing species and the exchange rate.[3] In view of the pK_a values of MQCN in the S_0 and S_1 states (-0.98 and 8.28, respectively[1]) we suggest that the proton transfer leading to the formation of IP occurs mainly in the S_1 state. Upon irradiation, the concentration of IP increases and hence the resultant band is expected to shift to a larger δ value. Such peak shift occurs also due to the heat accompanying UV irradiation (peak b is shifted due to the same reasons). After the light is cut off, the concentration of the ionic species is expected to decrease gradually and the resultant peak would correspondingly converge to the original position.

The enhanced absorptive CIDNP at peak δ=2.05 ppm is singlet and relaxes into a product peak at δ=1.95 ppm and assigned as the methyl group at position 4 of the transient product (T. Pr.), which by releasing HCN leads to the final product PEMQ; c.f. Scheme 1. Here, the Δg mechanism[4] is responsible for the absorptive CIDNP via the S-T_0 mixing in the RP2.

In conclusion, our results indicate the presence of at least two intermediate radical pairs; the first (RP1) is the radical pair involved in the back hydrogen transfer reaction and the second (RP2) is that leading to the final product monitored by Hata. Both enantiomers react through the same type of radical intermediates.

The present research was partly supported by a Grant-in-Aid for Scientific Research on Priority areas “Molecular Magnetism” (Area No. 228) No.04242102 and "Photoreaction Dynamics" (Area No. 249) No. 06239207.

References and Notes

1 N. Hata, *Chem. Lett.*, **1991**, 155; N. Hata, *Chem. Phys.*, **162**, 47(1992).
2 R. Kaptein and J. A. den Hollander, *Am. Chem. Soc.*, **94**, 6269(1972).
3 J. Sandström, Dynamic NMR Spectroscopy, p. 83, (Academic Press Inc. (London) Ltd, second print 1984).
4 See for example; a) R. Kaptein and L.J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195(1969); b) G.L. Closs, *J. Am.Chem. Soc.*, **91**, 4552(1969); c) F.G. Adrian, *J. Chem. Phys.*, **53**, 3918 (1971).