Triplex Promoted Intersystem Crossing of Ion–Radical pairs in the Photosensitized Valence Isomerization of Quadricyclane: Chemically Induced Dynamic Nuclear Polarization (CIDNP) Evidence

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Photosensitized valence isomerization of quadricyclane to norbornadiene by dibenzoylmethanatoboron difluoride in the presence of durene shows a CIDNP effect which is opposite in direction to that occurring in the absence of durene, demonstrating possible participation of triplexes in the durene co-sensitized reaction.

Triplexes have been invoked as viable intermediates in a variety of photochemical reactions.¹⁻³ However, the participation of triplexes in photoinduced electron transfer reactions has rarely been proved, because triplex emission could scarcely be detected either in polar solvents⁴ or in the case of two different quenchers.^{2,3} Recently, we⁵ found that the energetically unfavourable electron transfer isomerization of norbornadiene (NBD) to quadricyclane (QC) by a singlet sensitizer, dibenzoylmethanatoboron difluoride (DBMBF₂), could be accomplished by the addition of toluene, biphenyl or durene as a co-sensitizer, suggesting the involvement of triplexes in the process. We present herein further evidence of participation of triplexes in the reverse reaction, *i.e.* the valence isomerization of QC to NBD via photoinduced electron transfer in acetonitrile solvent, by means of chemically induced dynamic nuclear polarization (CIDNP), and discuss the role of the triplex in promoting intersystem crossing of ion-radical pairs.

It has been reported that DBMBF₂ sensitizes from its excited singlet state the photoisomerization of QC to NBD with high efficiency.⁶ Irradiation of DBMBF₂ with QC in [²H₃]acetonitrile gave rise in situ to polarized QC and NBD, i.e. emission for the cyclobutane protons (δ 1.5) and enhanced absorption for the bridgehead protons (δ 1.4) of QC, as well as enhanced absorption for the alkenic protons (δ 6.7) and emission for the bridgehead protons (δ 3.5) of NBD, together with line-broadening of DBMBF₂ [Fig. 1(a)].⁵ This CIDNP spectrum is totally opposite in direction to that reported by Roth $et al.^7$ for the (triplet sensitizer) chloranil-sensitized QC to NBD isomerization. Therefore, it indicates unambiguously that the polarized QC must come from the back electron transfer of singlet ion-radical pair (DBMBF₂·-/QC·+) and NBD must come from escaped QC⁺⁺ with a singlet exit channel (Scheme 1), according to the well-known Kaptein rule⁸ and the subsequent amendment.⁹[†] It has been proved previously that QC+ and NBD+ are distinct cation radicals7 and that the ion-radical pair (IRP) energy of DBMBF₂·-/QC·+ lies 9–11 kcal mol⁻¹ (1 cal = 4.184 J) above that of $\overline{DBMBF_2}$.-/NBD·+,⁵ rendering QC·+ easy to transform to NBD⁺. It is also obvious that the polarization of NBD derives from polarized QC+ because the hyperfine splitting constant of the bridgehead protons of OC⁺ has a relatively large positive value, whereas that of NBD⁺⁺ is very small and negative.⁵

Most strikingly, when durene (D) was added into the [²H₃]acetonitrile solution of DBMBF₂ and QC and irradiated in situ, the polarization directions were totally inverted, while the durene signal remained intact [Fig. 1(b)]. Because the polarization directions of both the in-cage recombination product (QC) and the escape product (NBD) were inverted, the only reasonable rationale for this polarization inversion must be alteration of the spin multiplicity of the IRP from singlet to triplet. In other words, participation of durene promotes intersystem crossing which facilitates the triplet recombination, leading to polarized triplet QC which, in turn, generates polarized QC. In addition, QC⁺ must escape out of the cage from a triplet IRP and rearrange to NBD+- in the bulk, then undergo electron transfer with QC to produce polarized NBD which causes the retention of polarization of $Q\dot{C}^{+}$ (Scheme 2). Another possibility, *i.e.* that QC⁺ escapes from the singlet IRP, rearranges to NBD⁺⁻ and then forms an F-pair with DBMBF₂⁻⁻ in the bulk, must be excluded. Although this mechanism could explain the emission polarization for the alkenic protons of NBD, it could not explain the absorption of the bridgehead protons. If the polarization did originate from the F-pair, namely NBD⁺⁺, the bridgehead protons should have shown negligible emission, as has been discussed previously.⁵ In addition, the



Fig. 1 80 MHz ¹H CIDNP spectra obtained during UV irradiation (with a Pyrex filter) of $[^{2}H_{3}]acetonitrile solutions of (a) DBMBF_{2} (0.02 mol dm⁻³)/QC (0.02 mol dm⁻³); (b) DBMBF_{2} (0.02 mol dm⁻³)/QC (0.02 mol dm⁻³)/D (0.03 mol dm⁻³); and (c) CN(0.02 mol dm⁻³)/QC (0.02 mol dm⁻³)/D (0.03 mol dm⁻³)$



Scheme 1 A = DBMBF₂. Arrows denote polarization directions.

F-pair mechanism cannot explain the concurrent inversion of the polarization direction of QC, which is undoubtedly an incage recombination product.

In order to check the role of durene, the 1-cyanonaphthalene (CN)-sensitized QC isomerization was re-investigated. It is known that singlet excited CN and 1,4-dicyanonaphthalene (DCN) form emissive exciplexes with alkylbenzenes,¹⁰ and QC quenches the exciplex fluorescence close to the diffusioncontrolled limit.² Pac et al. have proposed that triplexes are involved in the CN- or DCN-sensitized isomerization of QC in neat arenes or in cyclohexane solvent in the presence of arenes.² In acetonitrile, the isomerization probably proceeds via an electron transfer pathway with a much lower quantum yield than those in non-polar solvents, presumably owing to fast back electron transfer in the singlet radical-ion pair.¹¹ In this context, however, no CIDNP effect was detected during the CNsensitized isomerization of QC in acetonitrile. Roth and coworkers have proposed a mechanistic interpretation that both singlet and triplet recombination of the resulting ion-radical pair would regenerate QC and the complementary polarization components associated with these pathways would cancel each other.7

We confirmed the lack of polarization of the CN/QC system under conditions as reported.⁷ However, irradiation of a ternary mixture of CN, QC and durene (D) in $[^{2}H_{3}]$ acetonitrile resulted in an excellent CIDNP spectrum which is completely identical with that observed for the DBMBF₂/QC/D system [Fig. 1(*c*)]. A similar result was obtained when DCN was used in the place of CN. In view of Roth's suggestion,⁷ this CIDNP result clearly demonstrates that the participation of durene facilitates intersystem crossing of the ion–radical pair and/or prevents singlet back electron transfer, thus triplet recombination dominated the overall process.

Based on the above CIDNP results and in line with Pac's works,² the requirement of the modified ion-radical pair formation in generating the observed polarization dictates the intermediacy of the DBMBF₂/QC/D triplexes (or ternary ion-radical pairs) as shown in Scheme 2. The oxidation potential of durene (1.79 V *vs.* SCE) and the diffusion-limited quenching of DBMBF₂ fluorescence by durene (2.2×10^{10} dm³ mol⁻¹ s⁻¹) enables an exothermic electron transfer with DBMBF₂ ($\Delta G = -12.7$ kcal mol⁻¹⁵). In addition, the exciplex fluorescence of



Scheme 2 A = $DBMBF_2$, CN or DCN; D = durene. Arrows denote polarization directions.

DBMBF₂/durene can be efficiently quenched by QC, implying the involvement of the triplex. The concentrations used in the CIDNP experiments (*ca*. 0.02 mol dm⁻³ for each component) are high enough to ensure effective combination of the three components. Therefore, formation of an intermediate triplex is a logical conclusion. The participation of durene in the triplex may significantly stabilize the IRP by delocalizing the positive charge, and the insertion of durene between the sensitizer and QC in the IRP must facilitate the circumvention of the singlet back electron transfer, hence promoting the intersystem crossing that makes the triplet recombination pathway predominant.

In view of the fact that triplex emission is hardly observed in polar solvents, CIDNP experiments may afford a new approach for probing the intermediacy of triplexes in electron transfer reactions conducted in polar solvents. In addition, the triplexmediated photoinduced electron transfer reaction is expected to be used in other reactions to alter reaction channels.

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Footnote

† DBMBF₂ is a singlet sensitizer,⁶ thus μ is negative. The g value of QC⁺⁻ (*ca.* 2.0025¹²) is smaller than that of DBMBF₂⁻⁻⁻ (2.0033⁵), thus Δg is negative. The hyperfine splitting constants (hfc) of the cyclobutane protons and bridgehead protons of QC⁺⁻ are -10.5 and 7.9 gauss, respectively.⁵ Therefore, the emission of the cyclobutane protons and the enhanced absorption of the bridgehead ones mean that the polarized QC must be an incage product (ε is positive). The opposite polarization direction of the alkenic and bridghead protons of NBD predict that the polarized NBD must derive from escaped QC⁺⁻ (ε is negative) with a singlet exit channel (γ is positive).

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