

Return electron transfer in radical ion pairs of triplet multiplicity*

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Abstract: Return electron transfer (RET) in radical ion pairs may populate the reagent ground states or, in the case of triplet pairs, one reagent triplet state. The efficiency of triplet RET is governed by the free energies of singlet and triplet RET and by the topologies of the potential surfaces of parent molecules, radical ions, and accessible triplet states or biradicals. RET in triplet radical ion pairs is exemplified for two distinct relationships between the three potential surfaces.

Keywords: radical ion pairs; return electron transfer; triplet RET; topologies; potential surfaces.

INTRODUCTION: PHOTOINDUCED ELECTRON TRANSFER

Photoinduced electron transfer (PET) is a fundamental reaction type in excited-state organic chemistry. It occurs in solid state, solution, and gas phase, including the Earth's atmosphere and outer space [1]. The products can be supramolecular "charge-separated" entities (as in the photosynthesis of green plants), zwitterions, or ion pairs. In solution, PET serves as a versatile method for generating radical cation–radical anion pairs. PET utilizes the fact that the oxidative power of an acceptor and the reductive power of a donor are substantially enhanced by photo-excitation. Upon excitation of ground-state charge-transfer complexes, contact radical ion pairs (CRIPs) are formed, whereas electron transfer (ET) between an excited acceptor or donor and a complementary quencher usually gives rise to solvent-separated radical ion pairs (SSRIPs). The change in free energy for an electron-transfer reaction (ΔG_{ET}^0) is given by the excited-state energy (E^*), the one-electron redox potentials of acceptor and donor, $E_{(A^-/A)}^0$ and $E_{(D/D^+)}^0$, respectively, and a Coulomb term, $e^2/\epsilon a$ (eq. 1) [2]. The free energy of an SSRIP (i.e., the free energy difference between the radical cation–radical anion pair and the reagent ground states) is given by eq. 2 [2], whereas the pair energy relative to an accessible triplet or biradical (BR), $\Delta G_{\text{SSRIP,T}}^0$, is given by eq. 3.

$$-\Delta G_{\text{ET}}^0 = E^* + E_{(A^-/A)}^0 - E_{(D/D^+)}^0 + e^2/\epsilon a, \quad (1)$$

$$-\Delta G_{\text{SSRIP}}^0 = -E_{(D/D^+)}^0 + E_{(A^-/A)}^0 - [2.6 \text{ eV}/\epsilon - 0.13 \text{ eV}] \quad (2)$$

$$-\Delta G_{\text{SSRIP,T}}^0 = -E_{(D/D^+)}^0 + E_{(A^-/A)}^0 - [2.6 \text{ eV}/\epsilon - 0.13 \text{ eV}] + E_{(T, \text{BR})}^0 \quad (3)$$

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INTRA-PAIR RADICAL ION REACTIONS AND PROCESSES

Organic radical ions undergo many unimolecular (intra-ion), intra-pair, or bimolecular reactions. Intra-pair reactions include intersystem crossing (ISC), return electron transfer (RET), proton, atom or group transfer, or bond formation between the geminate radical ions. Intra-ion and intra-pair reactions can be quite fast. Still, bimolecular reactions can compete with them because of a spin multiplicity requirement for electron return or coupling reactions. Typically, only singlet pairs can recombine, whereas triplet pairs must undergo ISC before RET. The process of ISC is modulated by contributions from spin rotation, spin orbit coupling, the hyperfine interaction with strongly coupled nuclei, or differences in the electron g factors of the two radical ions [3–5].

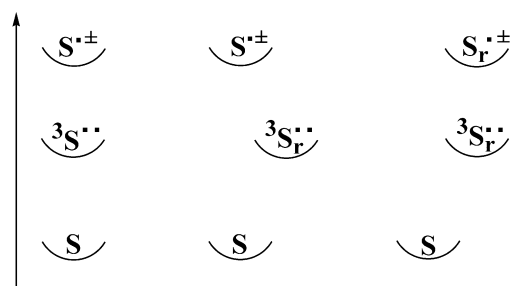
However, some ion pairs defy the dictate of singlet recombination. For example, laser excitation of anthracene or pyrene in the presence of *N,N*-diethylaniline generated “fast” triplets within the (~15 ns) laser excitation profile [6,7]. Formation on the ns time scale sets these triplets apart from triplets arising via diffusive encounters of independently generated radical ions.

RELATIONSHIPS BETWEEN POTENTIAL ENERGY SURFACES OF GROUND STATE, RADICAL IONS, AND TRIPLET STATE

Two factors govern the recombination of triplet radical ion pairs: the energetics of RET and the relationship between the potential surfaces of the parent molecules, their radical ions, and the accessible triplet or biradical species. The energetics determine the rate of RET and, thus, whether it will be competitive. The energetic requirements for triplet RET are subtle; RET can be very slow if the energy gap between E_T or E_{BR} and ΔG^0_{SSRIP} is either too large or too small (vide infra). Accordingly, triplet RET can be achieved by raising the ion pair energy (using sensitizers with higher reduction potentials) or by lowering it (using sensitizers with lower reduction potentials) [8,9]. The topologies of the various states influence the course of the overall reaction. If a radical ion and/or a triplet state or biradical have a geometry significantly different from that of the ground state or can rearrange to such a species, the sequence ET–RET may result in a rearrangement.

The potential energy surface of the reagent ground state can be related to those of radical ion and triplet state in three distinct ways. In simple cases, e.g., for aromatic donors and acceptors, the three potential surfaces have minima at related geometries (Scheme 1, left). In such cases, ET followed by RET does not cause rearrangement. A second case involves radical ions of strained ring systems ($S^{\bullet\pm}$), which may “relax” (rearrange) to ring-opened structures ($S_r^{\bullet\pm}$) of lower energy. In such systems, triplet states or biradicals (${}^3S_r^{\bullet\bullet}$) exist with connectivities related to the rearranged radical ions, but different from the ground state (Scheme 1, right). The most interesting case involves substrates whose radical ions resemble the parent, whereas triplet states or biradicals have a different connectivity (Scheme 1, center). For such reagents, RET will form triplet states or biradicals with newly formed or broken bonds relative to the ground state. In these cases, the sequence ET–RET may result in rearrangement. Representative examples of the three prototypes are described below.

The three ET–RET scenarios delineated above provide a natural as well as useful framework for the discussion of triplet RET. Representative examples of these prototypes are described below. The guiding principle in our discussion will be the relationship between potential surfaces rather than the method by which the mechanistic details were recognized or assigned.



Scheme 1 Schematic relationships between the potential surfaces of a substrate ground state (S), a radical ion ($S^{\bullet\pm}$ or $S_r^{\bullet\pm}$), and a related triplet/biradical ($^3S^{\bullet\bullet}$ or $^3S_r^{\bullet\bullet}$). The counter ions are chosen to have sufficiently high redox potentials to raise the pair energy above E_T .

POTENTIAL SURFACES OF SIMILAR GEOMETRIES

Aromatic donors or acceptors undergo only minor connectivity changes upon excitation to the triplet state or upon redox reactions. Because of large singlet–triplet gaps, the ISC of aromatics is typically slow. Triplet states can be populated in three steps: ET, ISC in the resulting ion pair, and RET in triplet pairs. Radical ions and triplet states of aromatics can be studied readily by optical spectroscopy; hence, the first observation of RET in the system pyrene/*N,N*-diethylaniline [6,7]. Interestingly, these triplet states were observed under conditions where essentially all excited-singlet pyrene was quenched and, therefore, population of the triplet state from the excited-singlet state could be excluded. Because the underlying mechanism was not understood, the claim of “fast triplets” by the amine donor was at first controversial [10].

The generation of fast triplets is now understood to arise by hyperfine-induced ISC in radical ion pairs. Nuclear spin states affect the precession frequencies of unpaired electrons in a magnetic field, accelerating or retarding the dephasing (i.e., ISC of radical ion pairs). Given a singlet precursor, the hyperfine mechanism accelerates ISC to triplet pairs, which recombine populating an accessible triplet state. Thermodynamic data (excitation energies, redox potentials) confirm that triplet RET is energetically feasible. The action of hyperfine-induced singlet–triplet mixing was confirmed by the magnetic field dependence of the triplet yield [11].

TRIPLET POTENTIAL AND RADICAL ION POTENTIAL SURFACES UNRELATED TO PARENT POTENTIAL SURFACE

In some substrates, the geometries of radical ion and triplet state are significantly different from the parent molecule, but related to each other. For example, radical cations of strained ring systems may rearrange, forming structures with relief of ring strain and/or extended conjugation; their rearrangement is facilitated due to significantly decreased activation barriers. In such systems, interesting conversions occur on the radical cation potential surface, and the resulting structures are conserved upon transition to the triplet/biradical.

For example, ET from 1,1-dianisyl-2-methylenecyclopropane, **1**, to chloranil (CA) generates a bifunctional radical cation, **2**^{•+}. Chemically induced dynamic nuclear polarization (CIDNP) effects (Fig. 1) show that the spin is localized in an allyl group, the charge in the diphenylmethylene function; the attachment of the diphenylmethylene moiety in the node of the allyl function does not permit further delocalization; a perfect bisected arrangement of the two units is not required [12]. The CIDNP effects support the formation of two CA-adducts and the regeneration of **1**. The signal directions indicate that reagent and adducts arise from pairs of different spin multiplicity, the adducts by coupling of singlet ion pairs, via zwitterions, **3**^{•+}, **4**^{•+}, the parent by triplet RET. However, the emission for **1** cannot

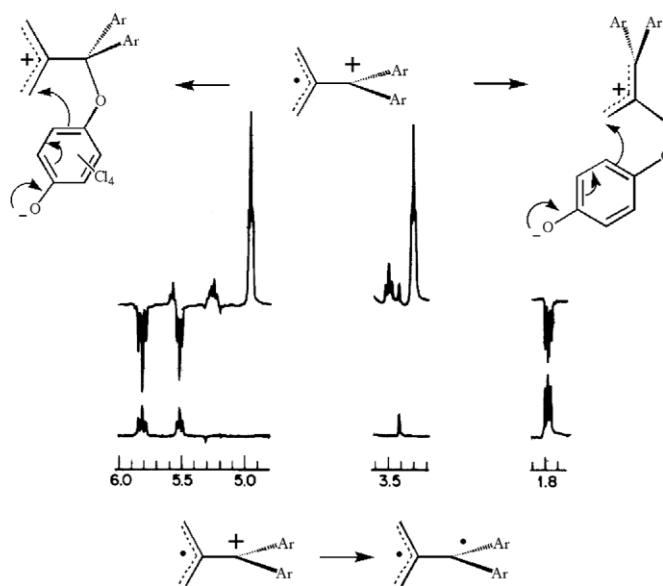
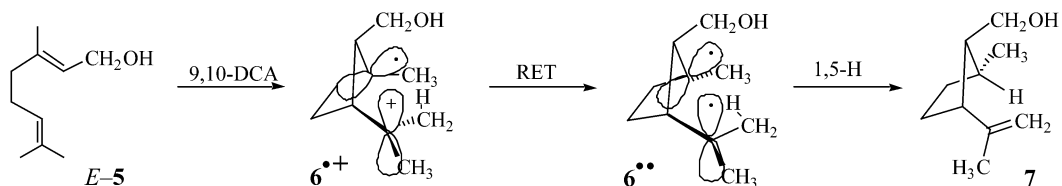


Fig. 1 CIDNP spectra observed during the photoreaction of CA with **1**. The emission signals at 1.8, 5.5, and 5.8 ppm represent **1** and are compatible with it being regenerated via triplet RET (below the spectra) [12,13]. Enhanced absorption signals at 3.3 and 4.9 ppm and at 3.6, 5.25, and 5.6 ppm identify the major and minor CA adducts, respectively, formed by coupling of singlet radical ion pairs via the major (top, right) and minor zwitterion (top, left) [12].

prove triplet RET conclusively. Because the polarization intensities of the adducts and of regenerated **1** are comparable, they must be generated on comparable time scales [12]. Additional studies, using ns laser flash and EPR spectroscopy and optoacoustic calorimetry, firmly establish the formation of the bisected biradical, **2^{••}**, by triplet RET [13].

The existence of a radical cation with an intact cyclopropane ring was probed by ion-molecule reactions in the gas phase. Donors of varying ionization potentials revealed the presence of two ions with electron affinities, $EA_{1^{•+}} = 8.44 \pm 0.05$ eV, $EA_{2^{•+}} = 7.41 \pm 0.05$ eV [14].

The radical cation of geraniol, *E*-3,7-dimethylocta-2,6-dien-1-ol, **E-5**, generated by PET to 1,4-dicyanobenzene or 9,10-dicyanoanthracene (9,10-DCA), undergoes a 5-center-C–C-cyclization to a di-tertiary, 2,α-bifunctional methyldene-cyclopentyl radical cation, **6^{•+}**. This species either undergoes intramolecular nucleophilic capture or, with 1,4-dicyanobenzene as sensitizer, is converted to *cis*-2-(2-propenyl)-*trans*-5-methylcyclopentanemethanol, **7**, with high stereospecificity. RET of the radical ion pair yields biradical, **6^{••}**, and a 1,5-H shift forms **7^{••}** [15]. Biradical, **6^{••}**, also undergoes cleavage of the doubly allylic C–C bond, regenerating **E-5**.



TRIPLET POTENTIAL SURFACE UNRELATED TO RADICAL ION OR PARENT

The most interesting relationship between the potential surfaces of parent, radical ion, and triplet/biradical involves substrates featuring a mismatch between the triplet potential surface and both ground-state and radical ion surfaces. The radical cations have geometries/connectivities related to the parent molecule, whereas the triplet state/biradical has a significantly different geometry. If RET is energetically feasible ($\Delta G^0_{\text{SSRIP}} > E_T$), one or several bonds must be broken or made as a direct result of the RET step.

In our typical approach, we separately probe two different features of these systems. The relationship between ground state and radical ion is delineated first. With this information in hand, we probe the relationship between triplet state and radical ion. The formation of quadricyclane, **9**, upon ET from norbornadiene, **8**, to 1-cyanonaphthalene serves as an illustrative example: a triplet state, **10^{••}**, is generated with formation of a new C–C bond [16,17].

The ET chemistry of the valence isomers, **8** and **9**, has attracted much attention. CIDNP experiments with **CA** established the existence of two distinct radical cations, **8^{•+}** and **9^{•+}**, each related uniquely to one precursor (Fig. 2, left) [16,17]. The structures of **8^{•+}** and **9^{•+}** are supported unambiguously by ab initio calculations [18], electron spin resonance (ESR) and electron–nuclear double resonance (ENDOR) data for **8^{•+}** [19], and ESR/chemically induced dynamic electron polarization (CIDEP) data for **9^{•+}** [20]. The bicyclic radical cation **8^{•+}** fails to undergo ring closure, whereas the quadricyclic radical cation **9^{•+}** produces **8** with a polarization pattern characteristic of **9^{•+}** (Fig. 2, left bottom) [16,17].

The ET reaction of **8** with 1-cyanonaphthalene (**1-CN**) generated polarized **8** and **9**, both with the polarization pattern characteristic of **8^{•+}** (Fig. 2, center). In this system, $\Delta G^0_{\text{SSRIP}} > E_T$ ($E^0_{\text{A}^-/\text{A}} = -1.98$ V vs. SCE; $E^0_{\text{D}/\text{D}^+} \sim 1.5$ V vs. SCE; $\Delta G^0_{\text{SSRIP}} \sim 3.5$ eV; $E_T \sim 2.8 - 2.9$ eV). Radical cation **8^{•+}** and the cyanoaromatic counter ion generate a triplet state [16,17], which likely has the nortricyclanediyl structure, **10^{••}**; the two electrons reside in two orbitals, bonding or anti-bonding between C2 and C6 [16,18]. This triplet, generated with formation of a new C–C bond, decays to **9**. The ET reactions of **8** and **9** were reinvestigated recently with additional sensitizers; this study confirmed the essential features of the previously delineated mechanism [16,17], adding the triplet energy of **10^{••}** based on optoacoustic calorimetry [21].

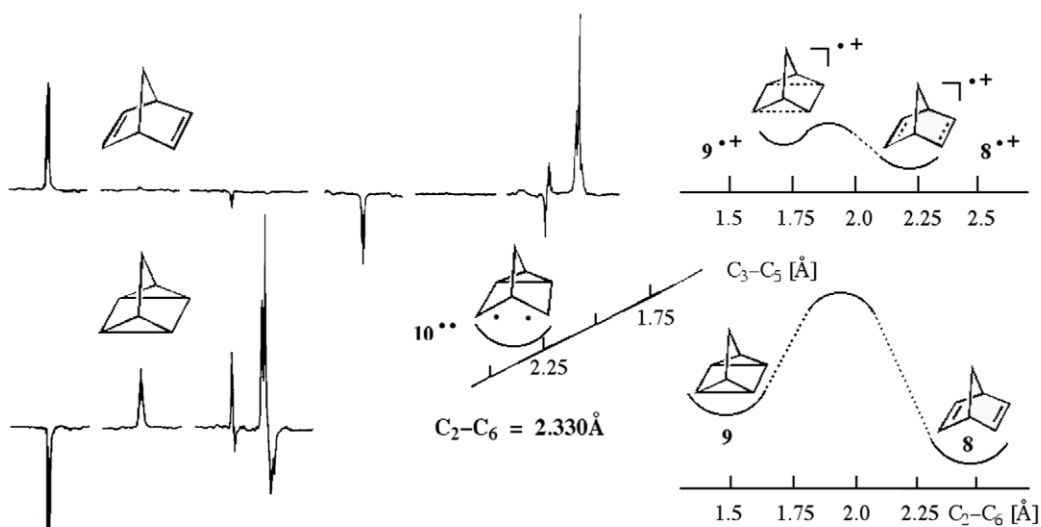
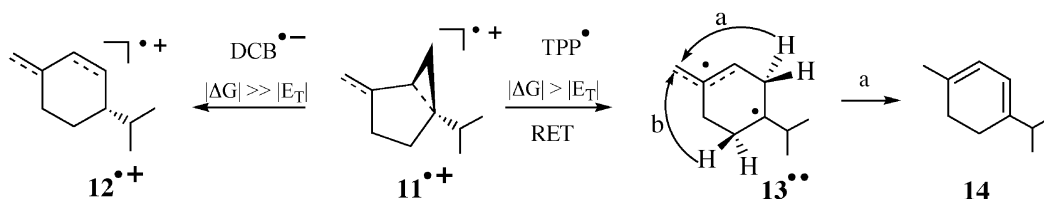


Fig. 2 CIDNP spectra during the reaction of **CA** with **8** (top, left) and **9** (bottom, left) and of **1-CN** with **8** (top, center) [16,17]. The energy diagram (right; vs. the C₂-C₆ length) shows a close relationship between parents and radical ions and the unique structure of biradical, **10^{••}**.

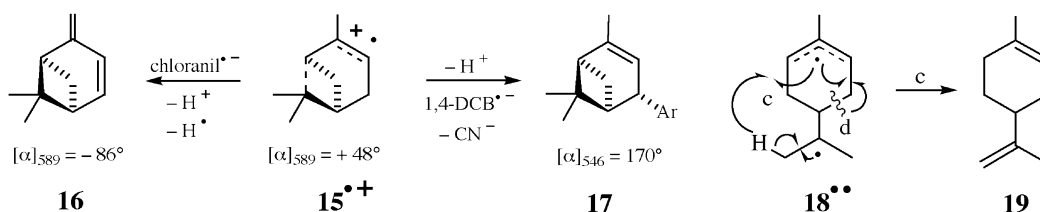
The bicyclic terpene sabinene (**11**) has a radical cation, **11^{•+}**, in which the stereochemical features of the parent are retained. With 1,4-dicyanobenzene (**DCB**) as sensitizer in acetonitrile, the radical cation, **11^{•+}**, undergoes a [1,3]-sigmatropic shift to β -phellandrene radical cation, **12^{•+}**, with inversion of configuration at the center bearing the isopropyl group [22]. In 5-M methanol **11^{•+}** undergoes nucleophilic capture with inversion at the quaternary carbon [22,23].

The sigmatropic shift was suppressed with triphenylpyrylium (**TPP⁺**) tetrafluoroborate as electron acceptor in favor of conversion to α -terpinene, **14**, and γ -terpinene (not shown) [9]. The two acceptors have identical excited-state reduction potentials (~ 2.7 eV, $-\Delta G_{ET}^0 \sim 1$ eV); thus, the radical cation, **11^{•+}**, should be formed with either sensitizer. On the other hand, the pair energy of [**11^{•+}**-**TPP^{•-}**], $\Delta G_{SSRIP}^0 \sim 1.8$ eV, lies significantly lower than that of [**11^{•+}**-**DCB^{•-}**], $\Delta G_{SSRIP}^0 \sim 3.1$ eV. [15] Accordingly, the pair [**11^{•+}**-**TPP^{•-}**] may populate a monocyclic biradical, **13^{••}**, by RET, regenerating **TPP⁺** in the process. Biradical **13^{••}** then decays by two competing H-migrations, forming **14** via pathway a and γ -terpinene via pathway b [9].



Similarly, α - and β -pinene, form radical cations (e.g., **15^{•+}**) in which the steric integrity of the four-membered ring is retained. For example, upon ET to CA **15** is converted to verbenene, **16**, with quantitative retention of optical purity [24]. The “ring-closed” nature of **18^{••}** also follows from the reaction of **15** with **DCB**, which generated three “substitution” products, in which a cyanophenyl group has replaced a H atom of **15**, all with high optical rotations [25].

Interestingly, irradiation of **DCB/15** in acetonitrile also produced significant yields of a monocyclic isomer, limonene, **19** (~ 50 %), and an acyclic isomer, ocimene, **20** (5 %; not shown) [25]. These products appear to be incompatible with the intermediacy of the ring-closed radical cation, **15^{•+}**, unless one considers triplet recombination. Triplet RET of the pair, **15^{•+}**-**DCB^{•-}** with ring opening forms the monocyclic 1,4-biradical, **18^{••}**, which generates **19** by a 1,5-H shift (c), and **20** by cleavage of the doubly allylic bond (d).



Perhaps the most interesting case of triplet RET involves the “ring-opened” triplet state formed from *cis*- or *trans*-1,2-diphenylcyclopropane radical cations (*cis*- or *trans*-**21^{•+}**). CIDNP effects observed during irradiation of chloranil in the presence of *cis*- or *trans*-**21** (Fig. 3, left) support radical cations with electron spin density on the benzylic carbons. Because *cis*- and *trans*-**21^{•+}** only regenerate starting material, these ions must have retained the steric integrity of their precursors [8,17].

In contrast, singlet acceptors, 1,4-dicyanonaphthalene (**DCN**) or 9-cyanophenanthrene (**9-CP**), react with *cis*- and *trans*-**21** causing isomerization, even though the polarization patterns support the same radical cations, *cis*- and *trans*-**21^{•+}** (Fig. 3, center), which did not rearrange with **CA**. Opposite

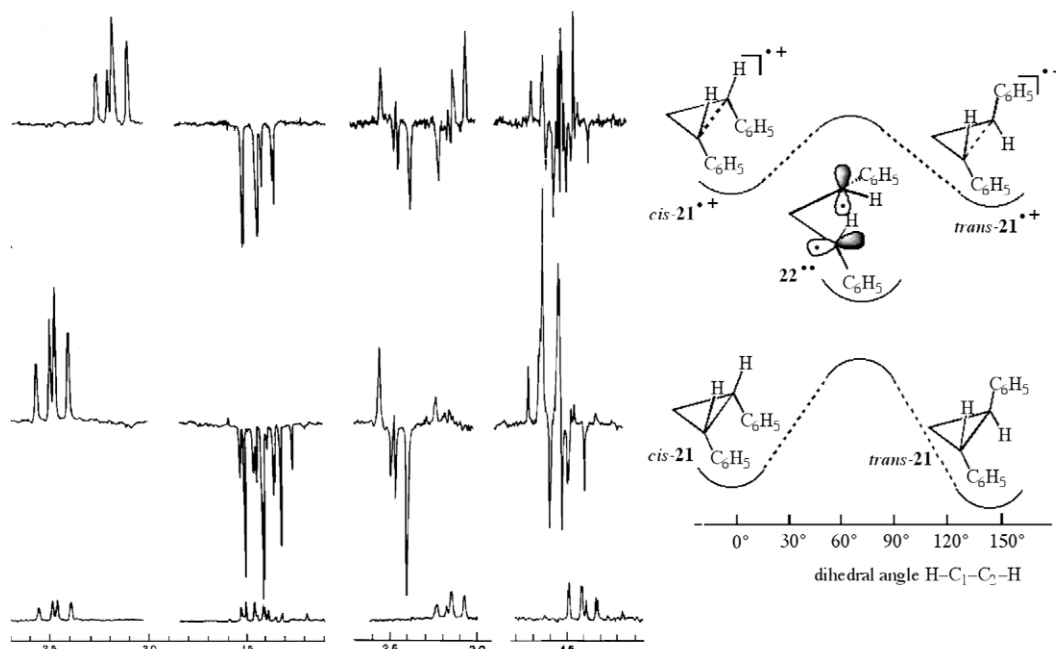


Fig. 3 CIDNP spectra observed during the reactions of CA with *cis*- (bottom, left) or *trans*-**21** (top, left) and of **DCN** (center, top) and **9-CP**, respectively, with *trans*-**21** (center, bottom) [8,17]. Key minima on the respective potential surfaces are compared on the right.

“multiplet effects” for reagent (E/A) and isomer (A/E; Fig. 3, center top), indicate that they are regenerated from ion pairs of different spin multiplicity. These results can be reconciled if two intermediates are involved consecutively, a radical ion, *cis*- or *trans*-**21**^{•+}, whose spin density pattern determines the polarization pattern, and a triplet state, which allows for the rearrangement [8,17].

The reduction potentials of **DCN** ($E_{A^-/A}^0 \sim -1.28$ V vs. SCE) or **9-CP** ($E_{A^-/A}^0 \sim -1.88$ V vs. SCE) place the free energies of the radical ion pairs generated with *cis*- or *trans*-**21** ($E_{D/D^+}^0 \sim 1.5$ V vs. SCE) in the range, $\sim 2.8 < |-\Delta G_{\text{SSRIP}}^0| < 3.3$ eV; this may not permit RET to the spectroscopic triplet state, but a ring-opened triplet species with orthogonal p-orbitals, viz., **22**^{••}, is accessible [8,17]. Structure **22**^{••} lies near a saddle point on the potential surface of *cis*- and *trans*-**21** and, thus, can decay to either isomer [8,17]. Concerning the structure of **22**^{••}, Hammond and coworkers had explained the triplet-sensitized isomerization of *cis*- and *trans*-**21** by a related triplet state: “An obvious mechanism for the reaction involves energy transfer with breaking of the weak C–C bond connecting the two ring members which bear the phenyl substituents” [26].

Comparing the CIDNP spectra obtained with **DCN** and **9-CP** (Fig. 3, center, top vs. bottom) reveals an interesting feature: the reaction with **DCN** produced a well-balanced polarization for reagent and isomer, whereas with **9-CP** the polarization of the rearranged product dominated. This is a highly significant observation, because it leads to the conclusion that triplet RET is more efficient than singlet RET [8,17].

RET to *cis*- or *trans*-**21** was reinvestigated recently with additional sensitizers. The principal contributions of this work are the free energy of the biradical, $E_{\text{BR}} = 29$ kcal mol⁻¹, assigned on the basis of optoacoustic calorimetry data, and the absorption spectrum of the previously established triplet state **22**^{••} [27]. Otherwise, this study led the authors to postulate once again the previously assigned mechanism [8,17]. Because the lifetime of the intermediate(s) preceding triplet **22**^{••} is very short (<100 ps), a detailed analysis of its decay and of the rise of **22**^{••} appears desirable. Notably, the direct formation of

biradical, 22^{**} , by (dissociative) triplet energy transfer (DTET) from the reagent triplet state was not investigated.

RATES OF RETURN ELECTRON TRANSFER

The rates of (charge-separating) ET and (charge-annihilating) RET reactions have been of major interest since Marcus formulated an ET theory as a function of the driving force, ΔG^0 , and a "solvent reorganization energy", λ_s . This theory includes the unexpected prediction that ET rates should reach a maximum for $\lambda_s = \Delta G^0$, and decrease at higher driving forces, in a striking deviation from classical Brønsted behavior [28]. The "inverted Marcus region" was confirmed for (charge-neutral) ET between radical anions and aromatic hydrocarbons in frozen solutions ($0.01 < |\Delta G^0| < 2.75$ eV) [29] and for intra-molecular ET in radical anions, [A-Spacer-B] $^{\bullet-}$, containing two acceptors linked by a spacer [30,31]. In ET reactions between cyano-substituted aromatic acceptors and methyl-substituted arene donors ($0.3 < |\Delta G^0| < 3.0$ eV) Gould, Farid, and coworkers established an inverted region for singlet-RET in solvent-separated as well as contact radical ion pairs (CRIPs) [32,33]. The resulting theoretical curve suggests that reaction free energies between 0.5 eV $< |-\Delta G^0_{SSRIP,T}| < 2.5$ eV allow for efficient RET, bridging the classical and the inverted region (cf., Fig. 4).

It is interesting to view some of the RET reactions discussed above in the light of the results of Gould, Farid, et al. Unfortunately, very little rate information is available for any of the systems discussed here, possibly due to the fact that the absorption spectra of most of these systems lie well below 350 nm and are not accessible by routine time-resolved spectroscopy. Qualitative evidence for "inverted Marcus" behavior can be derived for the reactions of sabinene, **11**; for the radical cation, **11 $^{+\bullet}$** , triplet RET becomes accessible by changing the sensitizer from **DCB** (high $|-\Delta G^0_{SSRIP,T}|$) to **TPP** (lower $|-\Delta G^0_{SSRIP,T}|$) [9,15].

CIDNP data can be used to derive rates of *appearance* of species generated via triplet RET (Fig. 4, filled squares, points 1, 9, 12) or singlet RET (filled circles, points 8, 14, 16). It is important to note that these data do not reflect the *intrinsic* RET rates, because the *effective* RET rates are limited by the process of spin sorting via hyperfine-induced ISC. Still, two CIDNP-derived rates provide valid information. First, Fig. 3, center bottom shows that for **9-CP $^{\bullet-}$ -21 $^{+\bullet}$** ($-\Delta G^0 = 3.5$ eV; Fig. 4, point 16) the

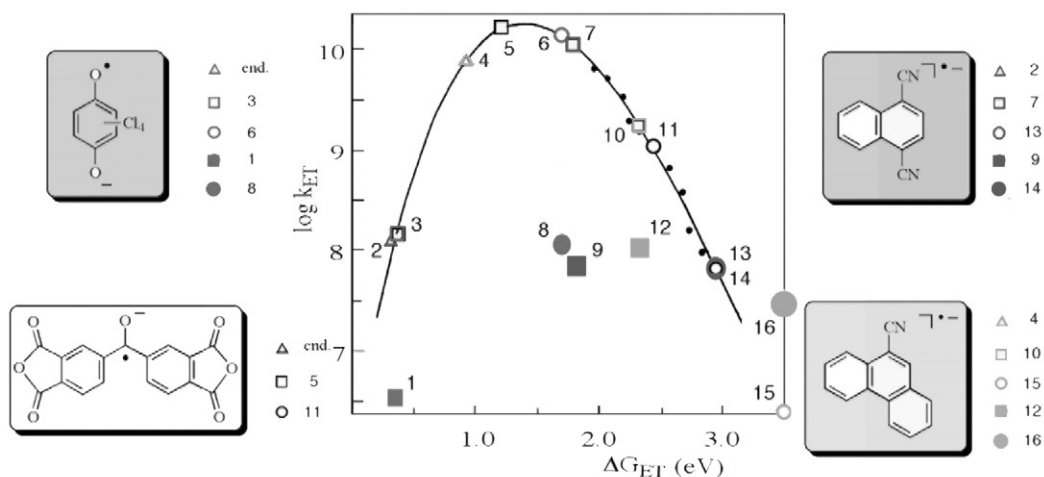


Fig. 4 CIDNP-derived rate constants for singlet RET (filled circles) and triplet RET (filled squares) from four radical anions to **21 $^{+\bullet}$** shown with data of Gould et al. for RET to alkylbenzene radical cations (small filled circles) [32]. Open circles, squares, and triangles denote rate constants for singlet RET, triplet RET, and RET to the spectroscopic triplet state, respectively, if these were to obey the Marcus curve of Gould et al. The projected rate of RET for [**DCN $^{\bullet-}$ - 21 $^{+\bullet}$**] (13) coincides with the actual one (14).

rate of singlet RET (which regenerates *trans*-**21**) is slower than that of ISC/triplet RET ($-\Delta G^0_{\text{SSRIP,T}} = 2.25$ eV; Fig. 4, point 12) by a factor of ~ 2 ; the low signal intensity is ascribed to a slow RET rate from the spin sorted pairs. Second, the triplet RET rate for $\text{CA}^{\bullet-} - \mathbf{21}^{\bullet+}$ ($-\Delta G^0_{\text{SSRIP,T}} = -0.35$ eV; point 1 is an *upper limit*) is well over one order of magnitude slower than ISC/singlet RET (point 8); clearly, triplet RET is not competitive.

It is informative to compare the CIDNP-derived rates with projected rates based on the theoretical curve of Gould et al. for RET to alkylbenzene radical cations [32]. We consider three RET processes: (a) singlet RET regenerating the reagent ground states (open circles, points 6, 11, 13, 15); (b) triplet RET generating the ring-opened $\mathbf{22}^{\bullet\bullet}$ (open squares, points 3, 5, 7, 10); and (c) triplet RET populating the spectroscopic triplet state, $\mathbf{21}^{\bullet\bullet}$ (open triangles, points 2, 4). The values of $-\Delta G^0$ used in this comparison were calculated according to eqs. 2 and 3.

These data suggest that the pair $[\text{DCN}^{\bullet-} - \text{trans-}\mathbf{21}^{\bullet+}]$ will undergo triplet RET to $\mathbf{22}^{\bullet\bullet}$ ($-\Delta G^0_{\text{SSRIP,T}} = 1.65$ eV; point 7) much faster than to $\mathbf{21}^{\bullet\bullet}$ ($-\Delta G^0_{\text{SSRIP,T}} = 0.35$ eV; point 2) in a ratio similar to that of singlet to triplet RET from the pair $[\text{CA}^{\bullet-} - \text{trans-}\mathbf{21}^{\bullet+}]$ (points 6 vs. 3). On the other hand, using the theoretical curve of Gould et al. to evaluate the pair $[\mathbf{9-CP}^{\bullet-} - \text{trans-}\mathbf{21}^{\bullet+}]$ suggests an advantage for RET to $\mathbf{21}^{\bullet\bullet}$ over $\mathbf{22}^{\bullet\bullet}$ (points 4 vs. 10). However, considering the significant increase in λ_s from CRIPs ($\lambda_s = 0.55$ eV) to SSRIPs ($\lambda_s = 1.6$ eV) [33], the Marcus curve, governing triplet RET to $\mathbf{21}^{\bullet\bullet}/\mathbf{22}^{\bullet\bullet}$, must be expected to be shifted to higher values of $|\Delta G^0|$, because the significant geometry change upon RET could result in an even higher value for λ_s in this case. The resulting shift of the Marcus curve would favor RET to $\mathbf{22}^{\bullet\bullet}$, while still favoring triplet RET from $\text{DCN}^{\bullet-}$ to $\mathbf{22}^{\bullet\bullet}$.

In light of these considerations, the energetics of at least the system $[\text{DCN}^{\bullet-} - \mathbf{21}^{\bullet+}]$ and possibly the system $[\mathbf{9-CP}^{\bullet-} - \mathbf{21}^{\bullet+}]$ are fully compatible with the direct generation of $\mathbf{22}^{\bullet\bullet}$ from *cis*- or *trans*- $\mathbf{21}^{\bullet+}$; this analysis fully bears out our original assignment [8,17]. Of course, the CIDNP patterns (Fig. 4, center) unambiguously support the conclusion that radical cations *cis*- and *trans*- $\mathbf{21}^{\bullet+}$ precede the ring-opened triplet. For chloranil [8,17] and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**BTDA**) [27], the population of the spectroscopic triplet state, $\mathbf{21}^{\bullet\bullet}$, is endergonic (end.) and, therefore, cannot be expected to compete. On the other hand, the triplet energy of **BTDA** lies sufficiently high to allow dissociative triplet energy transfer (DTET) generating $\mathbf{22}^{\bullet\bullet}$ without involving the radical cations as intermediates; exergonic triplet energy transfer has long been known to be quite fast [34,35]. The role of this process could be evaluated by a global analysis of the time-resolved spectra; this project has the potential to clarify many of the outstanding questions and to reconcile most, if not all, existing results. It would be particularly interesting to illuminate the role of DTET.

CONCLUSION

Triples RET has been established for radical ion pairs derived from a wide range of substrates. Of particular interest are systems where RET is accompanied by significant changes in structure, viz., in the conversions of $\mathbf{8}^{\bullet+}$ to $\mathbf{10}^{\bullet\bullet}$, $\mathbf{11}^{\bullet+}$ to $\mathbf{13}^{\bullet\bullet}$, $\mathbf{15}^{\bullet+}$ to $\mathbf{18}^{\bullet\bullet}$, and $\mathbf{21}^{\bullet+}$ to $\mathbf{22}^{\bullet\bullet}$. The acquisition of rate information is difficult (a) because the radical ions, $\mathbf{8}^{\bullet+}$, $\mathbf{11}^{\bullet+}$, and $\mathbf{15}^{\bullet+}$, and the triplet/biradical intermediates, $\mathbf{10}^{\bullet\bullet}$, $\mathbf{13}^{\bullet\bullet}$, and $\mathbf{18}^{\bullet\bullet}$, absorb in a spectral region that is not (yet) readily accessible, and (b) because they are typically formed in diffusion-controlled reactions and the intrinsic RET rates may be of comparable magnitude or faster. The high rates of exergonic triplet energy transfer [34,35] suggest that energy transfer from acceptor/sensitizer triplet states also may have to be considered.

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