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RADICAL CATIONS: GENERATION BY PHOTOCHEMICAL ELECTRON TRANSFER AND FRAGMENTATION

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Abstract

The high oxidizing power of excited states allows the preparation of radical cations in solution under mild conditions. These species often fragment competitively with back electron transfer and yield a radical and a cation. The selectivity of the process and the novel chemical reactions obtained is this ways are discussed through examples mainly using aryl nitriles as acceptors and benzyl derivatives as donors.

1. RADICAL IONS IN PHOTOCHEMISTRY

That radical ions have an important role in photochemistry and that new reactions of synthetic interest are obtained by photochemical electron transfer (PET) has become apparent in the mid-seventies with the pioniering work by D.R. Arnold on aromatic molecules, [1] and the recognizment of an electron transfer path in the photochemistry of ketones by S.D. Cohen [2] and P.J. Wagner [3] although the physical aspects of photoelectron transfer had been earlier under scrutiny [4-5]. Since then the concept of electron transfer has become popular in organic chemistry, and radical ions, formed photochemically [6-12] or thermally [11-13], are often invoked as intermediates in chemical reactions. Studies on photochemically generated radical ions have been devoted to their spectroscopic identification (flash photolysis [14] or epr [15]), or indirect identification via CIDNP [16], as well as to product studies. The

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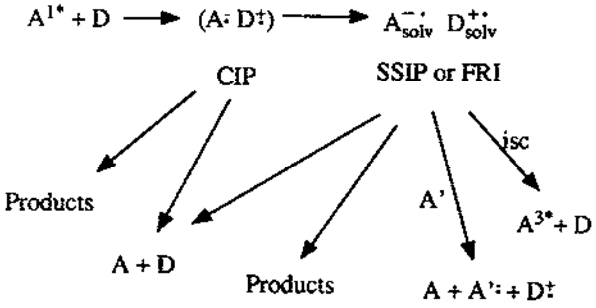
pertinent calculations are also being carried out [17-20].

In the present paper, we are mainly concerned with the cleavage of PET generated radical cations to yield radicals and with the ensuing chemistry of such species, and propose a unitary, if partly speculative, mechanistic scheme. The discussion is mainly based on our experience with arenenitriles as the excited acceptors.

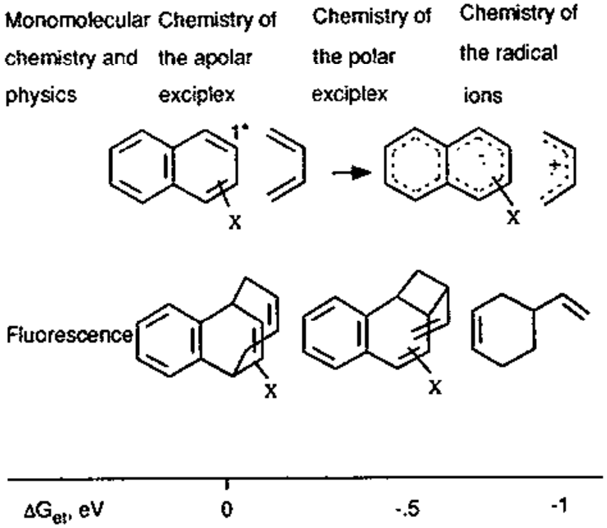
2. GENERAL ELECTRON TRANSFER SCHEME

We do not need to be much concerned with the general features of photoinduced electron transfer (Scheme I) since this has been adequately discussed elsewhere [6-11]. Efficiency of initial electron transfer is predicted on the basis of the Rehm-Weller equation [21], $\Delta G_{et} = F(E_{1/2}^{ox} - E_{1/2}^{red}) - E_{ex} + e_o^2/\epsilon a$, and checked, when using singlet excited acceptors, to which we are limited in the present discussion, by fluorescence quenching studies. It is now a familiar notion that excited states are both better reductants and better oxidants than the corresponding ground states, e.g. the singlet states of aromatic nitriles are very strong oxidants ($E_{1/2}^{red}(S^1) = E_{1/2}^{red} + E_{ex}(S^1)$ is for 1,4-dicyanobenzene 2.6, 1,2,4,5-tetracyanobenzene, 3.18, 1,4-dicyanonaphthalene 2.17 V vs SCE). This step generates the contact ion pair (CIP), with the radical ions probably in a high-energy Frank-Condon state, and is followed by relaxation to the solvent stabilized ion pair (SSIP) or the free solvated radical ions (FRI).



Scheme I

The CIP corresponds to the limit at high charge separation for the exciplex often invoked as an intermediate in photochemical cycloaddition processes [22-23]. Indeed, the degree of charge transfer affects the mode of cycloaddition observed and its efficiency [24-29], but when the free-energy change for electron transfer (determined by the parameters of both the molecules involved and the medium) is markedly negative cycloaddition ceases and other in cage chemical processes rarely compete [28–30] (see an example [29] in scheme II, see the last section for exceptions).



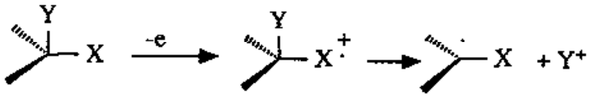
Scheme II

Thus the ions undergo separation and solvation. The rate of this process has be found to be near to 10^9 s^{-1} for several aromatic radical ion pairs and exciplexes [31–34], and is supposed not to change greatly when donors and acceptors of related structure are considered. This need not to be the case for different compounds, but it can be safely assumed that under the above conditions separation is fast and limits the CIP lifetime. In turn, decay of the free ions, apart from chemical reaction, involves secondary electron transfer, a key step in electron transfer photooxygenation [35], and in general a step which may increase the efficiency of the overall electron transfer photoinduced process [36], or reencounter with the counter ion resulting either in back electron transfer, and thus return to the ground state, or in inter system crossing generating the lowest-lying triplet [6].

The rate for back electron transfer depends on the ΔG of the process and, as it has been recently demonstrated, drops by several orders of magnitude in the "Marcus inverted region" [33]. In the cases discussed below the rate may vary between 10^8 s^{-1} to diffusion controlled. An increase in inter system crossing, e.g. in the presence of heavy atom containing additives limits the lifetime of the singlet radical ion pair [4], and may quench the reactions from it [37].

3. RADICAL IONS CLEAVAGE

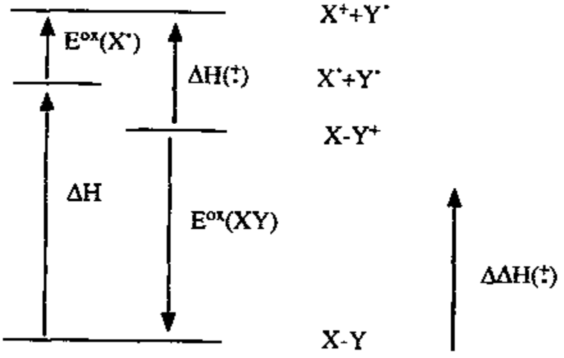
Electron exchange usually involves a localized moiety in the molecule of the donor (an aromatic nucleus,, an ether or amine function). Cleavage of a σ bond (whether carbon-hydrogen, carbon- carbon, or carbon-heteroatom) ß to it must then be considered, since it yields a stabilized radical [38-40].



(1)

$X = Ar, OR, NR_2$

More precisely, the bond dissociation enthalpy for the radical ion can be evaluated from the thermochemical cycle in Scheme III, from which it is apparent that the weakening induced by ionization is proportional to the difference between the oxidation potential of the neutral molecule and that of the radical corresponding to the ion formed [41-42]. Assuming the entropy term to be small, the enthalpy for the cleavage of the radical cation $XY^{\overset{+}{\cdot}}$ is estimated from eq. 2



Scheme III

$$\Delta H(\overset{+}{\cdot}) = \Delta H + F\,[E_{1/2}^{ox}(X^{\cdot}) - E_{1/2}^{ox}(X\text{-}Y)] \qquad (2)$$

Since radicals are easily oxidized and reduced, a conspicous lowering of the bond strength [$\Delta\Delta H(\overset{+}{\cdot})$] takes place.

$$\Delta\Delta H(\overset{+}{\cdot}) = \Delta H - \Delta H(\overset{+}{\cdot}) = F[E_{1/2}^{ox}(X\text{-}Y) - E_{1/2}^{ox}(X^{\cdot})] \qquad (3)$$

This effect may make the fragmentation of the radical cation fast enough to compete with back electron transfer. Such a condition may be met even for a substrate X-Y relatively hard to oxidize provided that the electrofugal group X corresponds to a radical easily oxidized, since it is the difference in eq. 3 which matters.

Furthermore the mode of fragmentation may be predicted, viz the preferred one of the possible fragmentations leads to the ion corresponding to the more easily oxidized radical. This refers both to the type of bond, e.g. the $\Delta H(^{+}_{\cdot})$ for the cleavage a C-H bond is generally larger than for a C-C bond since an alkyl radical is generally oxidized at a much higher potential than the hydrogen atom in solution, and the direction of the fragmentation, viz which fragment will become the radical and which one the ion, e.g. the radical cation of 2-methyl-1,1,2-triphenylpropane cleaves according to eq 4 and not to eq 4' since $PhCMe_2^{\cdot}$ in more easily oxidized than $Ph_2CH^{\cdot}$ (0.16 rather than 0.35 V vs SCE in acetonitrile) [40]

$$Ph_2CHCMe_2Ph^{+\cdot} \longrightarrow Ph_2CH^{\cdot} + PhCMe_2^{+} \qquad (4)$$

$$Ph_2CHCMe_2Ph^{+\cdot} \longrightarrow Ph_2CH^{+} + PhCMe^{\cdot} \qquad (4')$$

Some dissociation processes, the related bond dissociation enthalpy for the radical cation [$\Delta H(^{+}_{\cdot})$, kCal M^{-1}], and the weaking of the bond with respect to the neutral molecule [$\Delta\Delta H(^{+}_{\cdot})$] are exemplified below (Data obtained from the thermochemical cycle in fig. 1 [41-43]). The approximations involved in this approach are not discussed here). Proton transfer is an exothermic process for the toluene radical cation, as is general from the α-position of alkylated aromatics, while it is somewhat endothermic from the α position of amines.

$$PhCH_3^{+\cdot} \longrightarrow PhCH_2^{\cdot} + H^{+} \qquad \Delta\Delta H(^{+}_{\cdot})\ 105,\ \ \Delta H(^{+}_{\cdot}) -17 \qquad (5)$$

$$Me_2NCH_3^{+\cdot} \longrightarrow Me_2NCH_2^{\cdot} + H^{+} \qquad \Delta\Delta H(^{+}_{\cdot})\ 77,\ \ \Delta H(^{+}_{\cdot})\ 7 \qquad (6)$$

Indeed, the toluene radical cation is an extremely strong acid in acetonitrile (pK_a - 9 to -13) [18]. Generation of a benzyl radical is also obtained through the cleavage of a carbon-carbon bond when a suitable substitution makes the carbocation a convenient electrofugal group. Notice that e.g. an ether function in β weakens the bond more than a β-amino group does, since the lowering of the oxidation potential of the radical is more than compensated for by a similar decrease for the neutral molecule

$$Ph_2CHCH_2Ph^{+\cdot} \longrightarrow Ph_2CH^{\cdot} + PhCH_2^{+} \qquad \Delta\Delta H(^{+}_{\cdot})\ 41 \qquad (7)$$

$$Ph_2CHCH_2OMe^{+\cdot} \longrightarrow Ph_2CH^{\cdot} + MeOCH_2^{+} \qquad \Delta\Delta H(^{+}_{\cdot})\ 54 \qquad (8)$$

$$Ph_2CHCH_2NMe^{+\cdot} \longrightarrow Ph_2CH^{\cdot} + Me_2NCH_2^{+} \quad \Delta\Delta H(\overset{+}{\cdot})\ 48 \qquad (9)$$

In order to compete with other processes, notably back electron transfer (see above) such fragmentations must be at most slightly endothermic. Thus, in the following series of hydrocarbons, processes 11-13 are observed, but reaction 10 is not [41, 44-46].

$$PhCH_2CH_2Ph^{+\cdot} \longrightarrow PhCH_2^{\cdot} + PhCH_2^{+} \quad \Delta\Delta H(\overset{+}{\cdot})\ 39,\ \ \Delta H(\overset{+}{\cdot})\ 24 \qquad (10)$$

$$PhCH_2CMe_3^{+\cdot} \longrightarrow PhCH_2^{\cdot} + Me_3C^{+} \quad \Delta\Delta H(\overset{+}{\cdot})\ 57,\ \ \Delta H(\overset{+}{\cdot})\ 2 \qquad (11)$$

$$PhCMe_2CMe_2Ph^{+\cdot} \longrightarrow PhCMe_2^{\cdot} + PhCMe_2^{+} \quad \Delta\Delta H(\overset{+}{\cdot})\ 49,\ \ \Delta H(\overset{+}{\cdot})\ -3 \qquad (12)$$

$$Ph_2CHCHPh_2^{+\cdot} \longrightarrow Ph_2CH^{\cdot} + Ph_2CH^{+} \quad \Delta\Delta H(\overset{+}{\cdot})\ 38,\ \ \Delta H(\overset{+}{\cdot})\ 9 \qquad (13)$$

In all these cases proton transfer is exothermic, e.g. bibenzyl fragments according to eq. 14 rather the eq. 10 [45].

$$PhCH_2CH_2Ph^{+\cdot} \longrightarrow PhCH_2\dot{C}HPh + H^{+} \quad \Delta H(\overset{+}{\cdot})\ -21 \qquad (14)$$

However, it has been found that deprotonation mostly takes place with low efficiency [44,47], and thus is slow compared with back electron transfer. This depends on the unavailability of a suitable base for proton transfer. Radical anions (as opposed to dianions) are generally weak bases, and this is certainly true for arenenitriles [48-49]. Thus, proton transfer likely involves the solvent and when the cation radical is a carbon acid, it may be quite slow. The positive effect of secondary proton acceptors, e.g. traces of moisture [44] or added bases [50] (provided that they are not competitive as donor in the initial electron transfer) on the efficiency of such reactions supports this view.

This is not the case when the bond to be broken is more polar, e.g. proton transfer from the O-H group the radical cation of benzyl alcohols to the 1,4-dicyanonaphthalene (DCN) radical anion in fast [51] (and carbon carbon cleavage results as a secondary process).

$$DCN^{-\cdot} + PhCR(OH)CR(OH)Ph^{+\cdot} \longrightarrow DCNH^{\cdot} + PhCR(O^{\cdot})CR(OH)Ph \qquad (15)$$

$$PhCR(O^{\cdot})CR(OH)Ph \longrightarrow PhRC{=}O + Ph\dot{C}R(OH) \qquad (16)$$

Related processes (e.g. decarboxylation of phenylacetic acid [52], cleavage of α-aminoalchols initiated by proton transfer from the O-H group in the radical cation [53]) are similarly rationalized.

In the other cases, even if proton transfer is thermodynamically feasible, other fragmentations leading to delocalized cations are preferred, provided, of course, that they too are feasible. Thus, 1,1,2,2-tetraphenylethane undergoes carbon-carbon bond cleavage according to eq. 13 rather then the much more favourable deprotonation [$\Delta H(^{+\cdot})$ -29 kCal M^{-1}] [41,54].

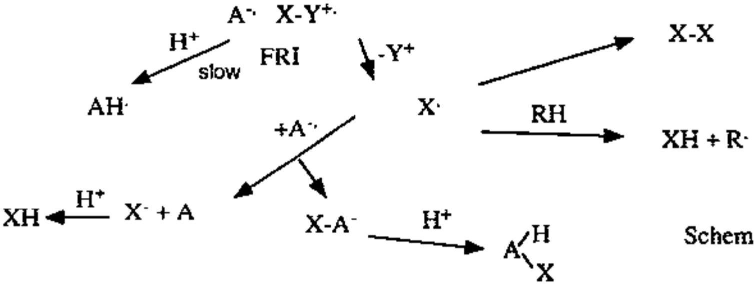
A carbon-carbon bond is easily fragmented also in ß-alkoxyethyl aromatic (compare eq. 8) [55] and aryloxirans [56] as well as acetals [57,58]. An organometallic cation is splitted off from the radical cations of benzylic silanes [54,59] stannanes [54, 59-61] and borates [62]. The mechanism of fragmentation does not need to be as simple as depicted in the above reactions, however. Thus cleavage of benzyltrimethylsilane radical cation occurs efficiently although it is predicted to be endothermic, since assistance by nucleophile attack onto the silicon atom provides an alternative pathway [62].

Fragmentation of benzyl radical cations requires that the bond to be cleaved is aligned with the π-cloud (compare eq. 1). This originates a selectivity due to conformational factors (e.g. deprotonation from the methyl rather than the iso-propyl group in cymenes, see again below, Scheme V) and the inefficiency of carbon-carbon cleavage in some rigid benzocycloalkanes [63].

Finally, here, and again in the next section, it is obvious that heterogeneization, i.e. the use of a solid material such as TiO_2 rather than a dissolved molecule as the excited acceptor greatly changes the observed chemistry [36,64], both because the donor reacts in the adsorbed state and because there is no molecular counterion, and likewise a change occurs when reactions of the radical ion pair, rather than of the solvated radical ions predominate (see last section).

4. SUBSEQUENT CHEMISTRY OF THE RADICALS.

The fate of the radicals obviously depend on their structure. As an example, α-amino radicals are easily oxidized to iminium cations [42,43,65,66] and ketyl radicals easily transfer a hydrogen atom [54] (a process obviously important when the sensitizer is a good hydrogen acceptor, e.g. a ketone) [3,66].

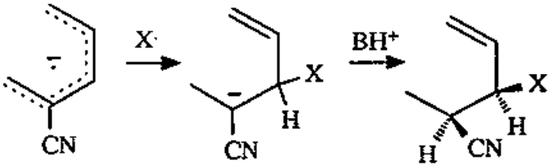


Scheme IV

Quite often, the radicals interact with the radical anion of the acceptor

(Scheme IV), and this takes either of the two courses. When the ground state acceptor is more difficult to reduce than the radical (easily reduced are e.g. benzhydryl and α-alkoxy radicals), then electron transfer ensues and the carbanion thus formed is protonated [41,67]. If the radical had been originally formed by deprotonation of a cation radical this corresponds to no net chemistry [67,68] (and this has been advanced as a rationalization for some observed inefficiencies), whereas if a different bond had been cleaved this path yields a fragmented hydrocarbon [41].

In the opposite case, addition takes place, and it is generally possible to switch from reduction to addition by changing from hard to reduce sensitizers, such as benzonitrile, dicyanobenzenes, monocyanonaphthalenes, to the more easily reduced polycyanobenzenes, -naphthalenes, or -anthracenes. In this way anionic adducts are formed and these either undergo loss of a cyanide group to give alkylaromatic (this is generally observed when rearomatization is the key factor, viz. when benzenenitriles are used, and results in formal substitution of an alkyl for a cyano group [69,71]) or reprotonation when the loss of aromaticity is less important viz. with naphthalene [44-46, 72-74] and anthracene nitriles [60,61,75]. Notice that, since in this case reprotonation of the anion is the last step of the sequence leading to the end products, stereoselectivity may results. Thus, from DCN only cis 2-alkyl-1,2-dihydro adducts are obtained [44,46,54], with a small percentage of the trans isomer only with bulky and stabilized alkyl radicals, e.g. diphenylmethyl [54] or p-methoxybenzyl [45,54].



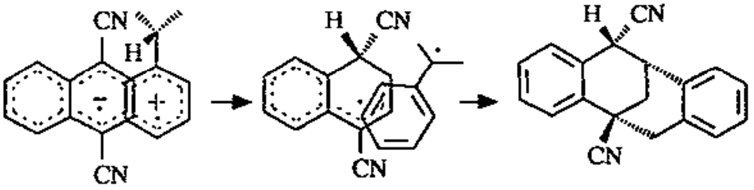
(19)

In this connection, it is interesting to note that alkyl radicals are obtained, besides than by cleavage of a σ bond, by addition of a nucleophile (e.g. methanol) to the radical cation of an alkene. Such a radical may, as before, add to the arene radical anion and a cyanide group be detached, thus originating the Nucleophile Olefin Combination-Aromatic Substitution process reported by Arnold [76].

Although the interaction between radicals and radical anions usually determines the course of the reaction, exceptions are possible, and these are when such species are either too reactive, e.g. with unsubstituted alkyl radicals some competition by hydrogen abstraction from the medium takes place [58], or too unreactive, due to sterical hindering or mesomeric delocalization. A typical example of "lazy" species pertaining to the latter group is the acenaphthenyl radical, which undergoes dimerization rather than addition to the 9,10-dicyanoanthracene (DCA) radical anion (and the latter in turn undergoes protonation in this case, see again Scheme IV) [77]. Reaction with other traps is also possible: e.g. PET induced oxygenation via reaction of benzyl radical with oxygen occurs efficiently [35,78].

5. CHEMISTRY OF THE RADICAL ION PAIR.

In the foregoing, the fragmentation process has been always considered to involve the "free" radical cation, a typical example being proton transfer to the solvent. However, in several cases there are indications of the chemical process occurring within the geminate radical ion pair before separation [53,61,79]. In particular, it may be pointed out to the reactions of DCN with alkylbenzenes, where direct proton transfer between the radical ions takes place within the solvent cage. This conclusion seems inescapable, though borne out only by products studies [44-46,54] (indeed it is difficult to think of a spectroscopic technique which would provide positive evidence for such a fast, in cage process). Thus, the reaction between DCN and toluene or other alkylbenzenes gives as the main products new tetracyclic adducts, with complete stereoselectivity (Scheme V).



CIP

Scheme V

No such process takes place when the radical arises through the detachement of a cation different from the proton or when the radical cation is too stable and rather diffuses (e.g. diphenylmethane [54], p-methoxytoluene [54,72], acenapthene radical cations [77]). Other indications for the in cage proton transfer are the following.

With α-D cumene, the label is transfered to the naphthalene moiety in position 1 [46]. The methyl-isopropyl selectivity when cymenes are used is completely different here than when the "free" radical cation deprotonates, and is well explained by short-range proton transfer in the sandwich complex, or CIP, where the isopropyl group is forced with the α proton parallel to the π orbital in contrast to what happens with the free ion [80,81].

The particular reaction course with this nitrile is rationalized on the basis of the enhanced basicity of DCN$^{\overline{\cdot}}$ as compared to other arenenitrile radical anions, in view of the higher localized charge in positions 1 and

4, the loss of aromaticity on protonation more tolerable than with the benzenenitriles, and the additional stabilization of the radicals DCNH$^{\cdot}$ by the second cyano group. The stereochemistry observed is explained admitting that in the sandwich complex the proton goes to the side of DCN opposed to the donor (on the side towards the donor proton transfer is easier but the more so is hydrogen transfer from DCNH$^{\cdot}$ back to the benzyl radical, Scheme V) [44]. Notice further that besides proton transfer, also transfer of an acetyl cation from a 3-amino-3-methylbutan-2-one derivative has been suggested to occur in the geminate pair [82].

6. CONCLUSIONS.

Recent studies have revealed much about the chemistry both of radical ions -hitherto rarely considered in organic chemistry- and of radicals in the particular setting provided by their generation through photochemical electron transfer - radical ion cleavage. Access to several identified pathways is determined by (and thus predicted on the basis of) redox parameters of the acceptor (in both ground and excited state), and of the donor, as well as the pK_a of the acceptor radical anion, and the bond dissociation energies in the radical cation. The striking decrease of the last quantity with respect to the neutral molecule is the most important factor, and opens a new way of generating radicals, the potential of which has been hardly explored to date. On the other hand, chemical reactions within the radical ion pair should not be underrated, though probably they are the exception rather than the rule. Indeed, in this cathegory new examples are found of the potential photochemical reaction have, of exploiting the sterochemistry of a weak association or conformational preferencesfor the regio- and stereoselective formation of covalent bonds.

7. REFERENCES.

1 R.A. Neunteufel and D.R. Arnold, J.Am.Chem.Soc., 95 (1973) 4080.
2 S.G. Cohen, A. Parola and G.H. Parson, Chem.Rev., 73 (1973) 141.
3 P.J. Wagner and R.A. Leavitt, J.Am.Chem.Soc., 95 (1973) 3669.
4a H. Leonhardt and A. Weller, Z.Elektrochem, 67 (1963) 791. (b) H. Leonhardt and A. Weller, Z.Phys.Chem (N.F.), 29 (1961) 277.
5 N. Mataga, T. Okada and N. Yamamoto, Chem.Phys.Lett., 1, (1967) 119.
6 M.A. Fox and M. Chanon (eds.) Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988.
7a G.J. Kavarnos and N.J. Turro, Chem.Rev., 86 (1986) 401. (b) G.J. Kavarnos, Top.Curr.Chem., 156 (1990) 21.
8 S.L. Mattes and S. Farid, Org.Photochem., 6 (1983) 233.

9a J. Mattay, Angew.Chem. i.e.e., 26 (1987) 285. (b) J. Mattay, Synthesis, (1989) 233.

10 A. Albini, Synthesis, (1981) 249.

11 L. Eberson, Electron Transfer Reactions in Organic Chemistry, Springer-Verlag, Berlin, 1987.

12 J.K. Kochi, Angew.Chem. i.e.e., 27 (1988) 1227.

13 N.L. Bauld, D.J. Bellville, B. Harirchian, K.T. Lorenz, R.A. Pabon, D.W. Rehynolds, D.D. Wirth, H.S. Chiou and B.K. Marsch, Acc.Chem.Res., 20 (1987) 371.

14a N. Mataga, Pure Appl.Chem., 56 (1984) 1255. (b) T.J. Burkey and D. Griller, Rev.Chem.Intermed., 5 (1984) 21.

15a F. Gerson, W. Huber, Acc.Chem.Res., 20 (1987) 85. (b) J.L. Courtneige and A.G. Davies, Acc.Chem.Res., 20 (1987) 90.

16 H.D. Roth, Acc.Chem.Res., 20 (1987) 343.

17 D.M. Camaioni, J.Am.Chem.Soc., 112 (1990) 9475.

18a A.M.P. Nicholas and D.R. Arnold, Can.J.Chem., 60 (1982) 2165. (b) X. Du, D.R. Arnold, R.J. Boyd and Z. Shi, Can J.Chem., 69 (1991) 1365.

19 D. Bellville, R. Pabon and N.L. Bauld, J.Am.Chem.Soc., 107 (1985) 4978.

20 D. Griller, J.A.M. Simoes, D. Mulder, B.A. Sim and D.D.M. Wayner, J.Am.Chem.Soc., 111 (1989) 7872.

21 H. Knibbe, D. Rehm and A. Weller,Ber. Bunsenges.Phys.Chem., 72 (1968) 257.

22 R.A. Caldwell and A. Creed, Acc.Chem.Res., 13 (1980) 45.

23 N.C. Yang, R.L. Yates, J. Masnovi, D.M. Shold and W. Chiang, Pure Appl.Chem., 51 (1979) 173.

24 A. Castellan, R. Lapouyade, H. Bouas-Laurent and J.Y. Lallemand, Tetrahedron Lett. (1975) 2467.

25 A. Albini, E. Fasani and D. Faiardi, J.Org.Chem., 52 (1987) 155.

26 T. Wolff, N. Müller and G. von Bünau, J.Photochem., 22 (1983) 61.

27 H. Bouas-Laurent and R. Lapouyade, J.Chem.Soc., Chem.Commun. (1969) 817.

28 J. Mattay, Tetrahedron, 41 (1985) 2393 and 2405.

29 A. Albini, E. Fasani and F. Giavarini, J.Org.Chem., 53 (1988) 5601.

30 F.D. Lewis, Acc.Chem.Res., 12 (1979) 152.

31 N. Mataga, T. Okada, Y. Kanda and H. Shioyama, Tetrahedron, 42 (1986) 6143.

32a J.L. Goodman and K.S. Peters, J.Am.Chem.Soc., 107 (1985) 6459. (b) J.L. Goodman and K.S. Peters, J.Am.Chem.Soc., 108 (1986) 1700.

33a I.R. Gould, R. Moody and S. Farid, J.Am.Chem.Soc., 110 (1988) 7242. (b) I.R. Gould, D. Ege, J.E. Moser and S. Farid, J.Am.Chem.Soc., 112 (1990) 4290.

34 A. Weller, Z.Phys.Chem. (N.F.), 130 (1982) 129.

35a L. Lopez, Top Curr.Chem., 156 (1990) 117. (b) M.A. Fox, in ref. 6, vol. D, 1.

36 M. Fox, Adv.Photochem., 13 (1986) 237.

37 M. Mella, E. Fasani and A. Albini, Tetrahedron, 47 (1991) 3137.

38 A. Albini and A. Sulpizio, in ref. 6, vol. C, 88.

39 N.J. Pienta, in ref. 6, vol. C, 421.

40 F.D. Saeva, Top Curr.Chem., 156 (1990) 59.

41 R. Popielarz and D.R. Arnold, J.Am.Chem.Soc., 112 (1990) 3068. (b) D.R. Arnold and L.J. Lamont, Can.J.Chem., 67 (1989) 2119. (c) A. Okamoto, M.S. Snow and D.R. Arnold, Tetrahedron, 42 (1986) 6175.

42 D.D.M. Wayner, J.J. Dannenberg and D. Griller, Chem.Phys.Lett., 131 (1986) 189.

43 D.D.M. Wayner, D.J. McPhee and D. Griller, J.Am.Chem.Soc. 110 (1988) 132.

44 A. Albini, E. Fasani and A. Sulpizio, J.Am.Chem.Soc., 106 (1984) 3562.

45 A. Albini, E. Fasani and E. Montessoro, Z.Naturforsh, 29b (1984) 1409.

46 A. Albini, E. Fasani and M. Mella, J.Am.Chem.Soc., 108 (1984) 4119.

47a F.D. Lewis, Acc.Chem.Res., 19 (1986) 401. (b) F.D. Lewis and J.R. Petisce, Tetrahedron, 42 (1966) 6207.

48 V.D. Parker, M. Tilset and O. Hammerich, J.Am.Chem.Soc., 109 (1987) 7905.

49 A. Gennaro, A.M. Romanin, M.G. Severin and E. Vianello, J.Electroanal.Chem., 169 (1984) 279.

50 D.R. Arnold, and S.A. Mines, Can.J.Chem., 67 (1989) 689.

51 A. Albini and M. Mella, Tetrahedron, 42 (1966) 6219.

52 J. Libman, J.Am.Chem.Soc., 98 (1976) 5931.

53a X. Ci and D.G. Whitten, J.Am.Chem.Soc., 109 (1987) 7215. (b) X. Ci, L.Y.C. Lee and D.G. Whitten, J.Am.Chem.Soc., 109 (1987) 2536.

54 A. Sulpizio, A. Albini, N. d'Alessandro, E. Fasani and S. Pietra, J.Am.Chem.Soc., 111 (1989) 5773.

55 D.R. Arnold and A.J. Maroulis, J.Am.Chem.Soc., 98 (1976) 5931.

56 A. Albini and D.R. Arnold, Can.J.Chem., 56 (1978) 2985.

57 D.R. Arnold and L.J. Lamont, Can.J.Chem., 67 (1989) 2119.

58 M. Mella, E. Fasani, A. Albini, J.Org.Chem., 57 (1992) 3051.

59 K. Mizuno, K. Terasaka, M. Yasueda and Y. Otsuji, Chem.Lett., (1988) 145.

60 D.F. Eaton, J.Am.Chem.Soc., 103 (1982) 7235.

61 J.P. Dinnocenzo, S. Farid, J.L. Goodman, I.R. Gould, W.P. Todd and S.L. Mattes, J.Am.Chem.Soc., 111 (1989) 8973.

62 J.Y. Lan and G.B. Schuster, J.Am.Chem.Soc., 107 (1985) 6710.

63 D.R. Arnold, B.J. Fahie, L.J. Lamont, J. Wierzchowski and K.M. Young, Can.J.Chem., 65 (1987) 2734.

64 P. Pichat and M.A. Fox, in ref. 6, Vol. D, 241.

65a X. Ci, R.S. da Silva, J.L. Godwin, D.E. Nicodem and D.G. Whitten, J.Am.Chem.Soc., 110 (1988) 8548. (b) W. Xu, Y.T. Jean, E. Hasegawa, U.C. Yoon and P.S. Mariano, J.Am.Chem.Soc., 111 (1981) 413.

66 X.Ci, R.S. da Silva, D. Nicodem and D.G. Whitten, J.Am.Chem.Soc., 111 (1989) 1337.

67 N. d'Alessandro, E. Fasani, M. Mella, L. Toma and A. Albini,

Tetrahedron,47 (1991) 5043.

68 X. Ci and D.G. Whitten, D.G., J.Am.Chem.Soc., 111 (1989) 3459.

69 A. Yoshino, M. Ohashi and T. Yonezawa, J.Chem.Soc., Chem.Commun., (1971) 97.

70 M. Ohashi and K. Miyake, Chem.Lett., (1977) 615.

71 M. Ohashi, K. Tsujimoto, Y. Kurukawa, J.Am.Chem.Soc., Perkin Trans. 1, (1979) 1147.

72 A. Albini and S. Spreti, Tetrahedron, 40 (1984) 2975.

73 A. Albini, E. Fasani and R. Oberti, Tetrahedron, 38 (1982) 1034.

74 N. d'Alessando, E. Fasani, M. Mella and A. Albini, J.Chem.Soc., Perkin Trans. 2, (1991) 1977

75 E. Hasegawa, M.A. Brumfield and P.S. Mariano, J.Org.Chem., 53 (1988) 5435.

76a D.R. Arnold, X. Du, J.Am.Chem.Soc., 111 (1989) 7666. (b) D.R. Arnold, and M.S. Snow, Can.J.Chem., 66 (1988) 3012.

77 E. Boggeri, E. Fasani, M. Mella and A. Albini, J.Chem.Soc., Perkin Trans. 2, (1991) 2097.

78a A. Albini and S. Spreti, J.Chem.Soc. Perkin Trans 2, (1987) 1175. (b) A. Albini and S. Spreti, Z.Naturforsh, 41b (1986) 1286.

79 M.A. Kellett and D.G. Whitten, J.Am.Chem.Soc., 111 (1989) 2314.

80 A. Albini and A. Sulpizio, J.Org.Chem., 54 (1989) 2147.

81 A. Sulpizio, M. Mella and A. Albini, Tetrahedron, 45 (1989) 7545.

82 W.R. Bergmark and D.G. Whitten, J.Am.Chem.Soc., 112 (1990) 4042.