DEDIAZONIATION OF ARENE DIAZONIUM SALTS BY TRIPLET EXCITED AROMATIC KETONES: ELECTRON OR ENERGY TRANSFER?[†]

H. BAUMANN, H. G. O. BECKER, K. P. KRONFELD, D. PFEIFER and H.-J. TIMPE

Chemistry Section, Technical University Leuna-Merseburg, DDR-42 Merseburg (G.D.R.)

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Summary

The triplet excited aromatic ketones benzophenone, xanthone, thioxanthone, fluorenone, benzil and 4,4'-dimethoxybenzophenone sensitize the dediazoniation of arene diazonium salts. The quantum yields of the photolyses of benzene diazonium tetrafluoroborate in the presence of these ketones and of 4-chlorobenzene diazonium tetrafluoroborate, 4-methylbenzene diazonium tetrafluoroborate and 4-methoxybenzene diazonium tetrafluoroborate in the presence of benzophenone were determined. In almost all cases the reduction products are of the Ar—H type (Ar ≡ aryl) which is characteristic of the electron transfer mechanism. The photochemically induced dynamic nuclear polarization (photo-CIDNP) of 4-chlorobenzene diazonium tetrafluoroborate and 4-cyanobenzenediazonium-β-^{15}N tetrafluoroborate in the presence of the ketones under investigation was also studied. In all cases except fluorenone the signs of the photo-CIDNP effects clearly point to triplet precursors. The photo-CIDNP effect in the presence of fluorenone has the same sign as that of pyrene which is known to react via the excited singlet state. This is because of the long lifetime of the excited singlet state of fluorenone which is efficiently trapped by the diazonium salt. These results suggest that the dediazoniation of arene diazonium salts sensitized by aromatic ketones proceeds via electron transfer but not via energy transfer.

1. Introduction

It has been known since 1974 that the photochemical dediazoniation of arene diazonium salts can be spectrally sensitized by aromatic hydrocarbons [1] or xanthene dyes [2]. These reactions start from the singlet excited sensitizer and proceed via electron transfer as has been shown by the determination of the sensitizer cation radical formed on electron transfer [1] and by studies of photochemically induced dynamic nuclear polarization

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[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

(photo-CIDNP) [3]. In addition much discussion has been devoted to the problem of whether arene diazonium salts can also react via their triplet excited states.

The absence of a heavy atom effect in the photolysis of arene diazonium salts [4], symmetry considerations [5] and the results of quantum-chemical calculations [6, 7] suggest that triplet reactions or dediazoniations of arene diazonium salts sensitized by triplet energy transfer do not occur. Scaiano and Kim-Thuan [8] have recently published rate constants for the quenching of excited triplet states of typical ketone triplet sensitizers by diazonium salts and have discussed the results in terms of triplet energy transfer. However, it is known that triplet excited dyes spectrally sensitize the dediazonia-tion of arene diazonium salts with high efficiency via electron transfer [9]. These results cast some doubt on the conclusions of Scaiano and Kim-Thuan.

In the present paper the problem is studied by means of photo-CIDNP experiments, quantum yield measurements and product analyses.

2. Experimental details

Xanthone, thioxanthone, fluorenone and 4,4'-dimethoxybenzophenone (DMBP) were synthesized according to standard procedures [10 - 13]. Benzo-phenone, benzil and pyrene were pure commercial products. All compounds were repeatedly recrystallized and finally sublimed. The synthesis of the arene diazonium salts and the procedure for performing the photo-CIDNP measurements are described in ref. 14.

The quantum yields of dediazoniation were determined by measuring the nitrogen evolved in a 9:1 (by volume) acetonitrile—water mixture contain-ing 10^{-2} M ketone and 10^{-2} M $ArN_2^+ BF_4^-$ (Ar $\equiv$ aryl) on irradiation at 365 nm (the absorption was almost exclusively by the ketone). The dediazo-niation products were determined by gas—liquid chromatography as described earlier [15]. The fluorescence lifetimes were determined using an LIF 200 laser impulse fluorometer (ZWG, Academy of Sciences of the G.D.R.) com-bined with an MC 80 microcomputer (VEB Elektronik, Gera). A resolution of about 300 ps could be obtained by deconvoluting the signals. The fluores-cence spectra were obtained using standard methods.

Oxygen-free argon was bubbled through the solutions for 20 min prior to determination of the quantum yields, the dediazoniation products and the phosphorescence spectra. The CIDNP spectra were measured on solutions which had not been deaerated.

3. Results

When the ketones are excited in the presence of benzene diazonium tetrafluoroborate in an acetonitrile—water mixture high quantum yields of nitrogen and the homolytic dediazoniation product benzene are obtained

TABLE 1

Photophysical and photochemical data for the sensitizers used in this work and their reactions with benzene diazonium tetrafluoroborate

Sensitizer	BP	X	TX	F	Bz	DMBP	Py
E_T (eV)	3.0	3.2	2.8	2.3	2.4	3.0	2.1
E^{ox} [a] (V (SCE))	2.3	1.8	1.67[b]	1.7	2.0	1.0	1.2
ϕ_{ISC}° [c]	1.0	—	1.0	0.93	0.92	—	0.38
τ_0^s (ps)	8[d]	8.5[d]	1050[e] 5600[f]	17000[e]	2000[e]	6.5[d]	300000
τ_0^t (μs)	14.3[g]	17.9[h]	73[i]	29[j]	59[k]	—	—
Φ_{N_2}	0.37	0.33	0.10	0.02	0.10	0.43	0.38[l]
Φ_{ArH}	0.37	0.32	0.09	0.02	0.08	0.40	—
k_q^s ($\times 10^9\,M^{-1}\,s^{-1}$)	—	—	8.5[m]	8.6[m]	—	—	20
k_q^t ($\times 10^9\,M^{-1}\,s^{-1}$)	3.8[n]	9.8[n]	—	—	1.0[m,o]	—	—
E_{rp} (eV)	2.0	1.5	1.4	1.4	1.7	0.7	—
$^3\Delta G_e^{\circ}$	−1.1	−1.7	−1.4	−0.9	−0.7	−2.3	—

BP, benzophenone; X, xanthone; TX, thioxanthone; F, fluorenone; Bz, benzil; Py, pyrene; DMBP, 4,4'-dimethoxybenzophenone.

[a] Calculated from the ionization energies using eqn. (4) unless otherwise stated.
[b] Measured in acetonitrile [16].
[c] From ref. 17.
[d] Measured in benzene [18].
[e] Measured in acetonitrile (this work).
[f] Measured in a 9:1 (by volume) acetonitrile–water mixture (this work).
[g] From ref. 19.
[h] Measured in a 9:1 (by volume) water–ethanol mixture (this work).
[i] From ref. 20.
[j] From ref. 21.
[k] From ref. 22.
[l] The coincidence with ϕ_{ISC}° is fortuitous because $\phi_{ISC}^{\circ} \approx 0$ at $[PhN_2^+BF_4^-] = 2.5 \times 10^{-2}$ M.
[m] Measured in a 1:1 (by volume) acetonitrile–water mixture.
[n] From ref. 8.
[o] In ref. 8 $k_q^t = 2 \times 10^6$; the reason for this discrepancy is not clear.

(Table 1). Similar quantum yields are obtained with substituted benzene diazonium salts: 4-chlorobenzene diazonium tetrafluoroborate, 0.39; 4-methylbenzene diazonium tetrafluoroborate, 0.16; 4-methoxybenzene diazonium tetrafluoroborate, 0.15.

The rate constants k_q^s and k_q^t of the quenching of the singlet and triplet excited states respectively of the aromatic ketones by benzene diazonium tetrafluoroborate were determined by Stern–Volmer treatment of the emission intensities measured in a 9:1 acetonitrile–water mixture. The pertinent data are summarized in Table 1. The rate constant k_q^t for the thioxanthone–diazonium salt system could not be evaluated owing to the very low phosphorescence intensity of thioxanthone. Flash photolysis experiments were not successful because a transient is formed whose absorption band cannot be separated from the triplet absorption band.

When 4-chlorobenzene diazonium tetrafluoroborate or 4-cyanobenzene diazonium-β-^{15}N tetrafluoroborate was photolysed in the presence of an aromatic ketone within the probe compartment of a pulse Fourier transform—nuclear magnetic resonance (PFT—NMR) spectrometer (Bruker HX 90-R operating in the ^{13}C or ^{15}N regime) the re-formed diazonium salts (cage products) and the excape product [15]N≡N were found to emit strong CIDNP signals. Typical examples are shown in Figs. 1 and 2. The CIDNP data are summarized in Table 2 which also contains the results obtained with the singlet electron transfer sensitizer pyrene [5, 14, 15] for comparison.

4. Discussion

The CIDNP technique is probably the best method available at present for demonstrating the existence of electron transfer mechanisms and for differentiating between electron transfer and energy transfer in which, at best, secondary polarizations resulting from the triplet polarization mechanism
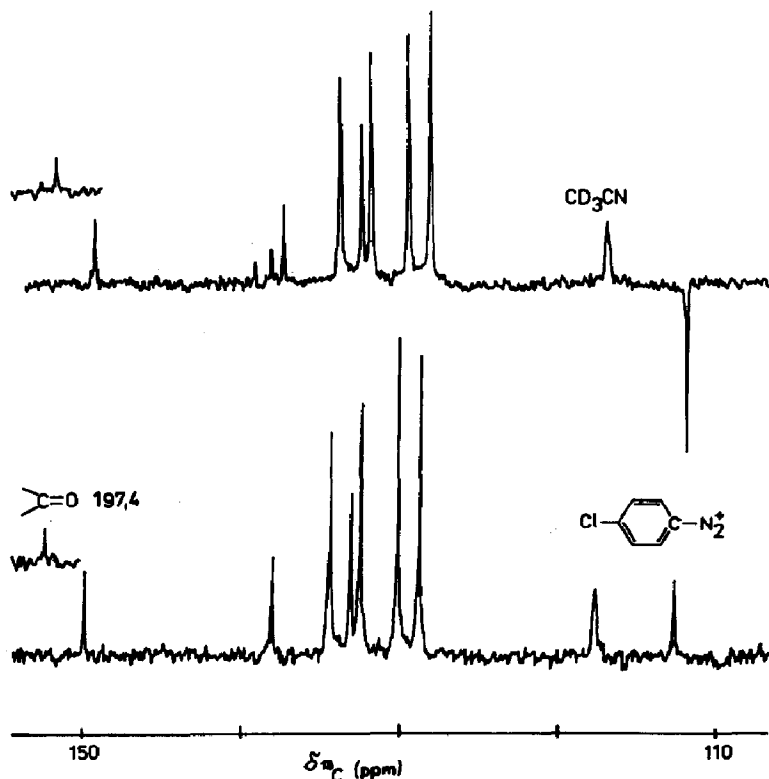

Fig. 1. [13]C {[1]H} photo-CIDNP spectrum at 22.635 MHz of a solution of 0.5 M 4-chlorobenzene diazonium tetrafluoroborate and 0.1 M benzophenone in acetonitrile-d_3: upper curve, λ_{exc} > 300 nm; lower curve, normal nuclear magnetic resonance spectrum of the system. 100 scans were taken for each curve.
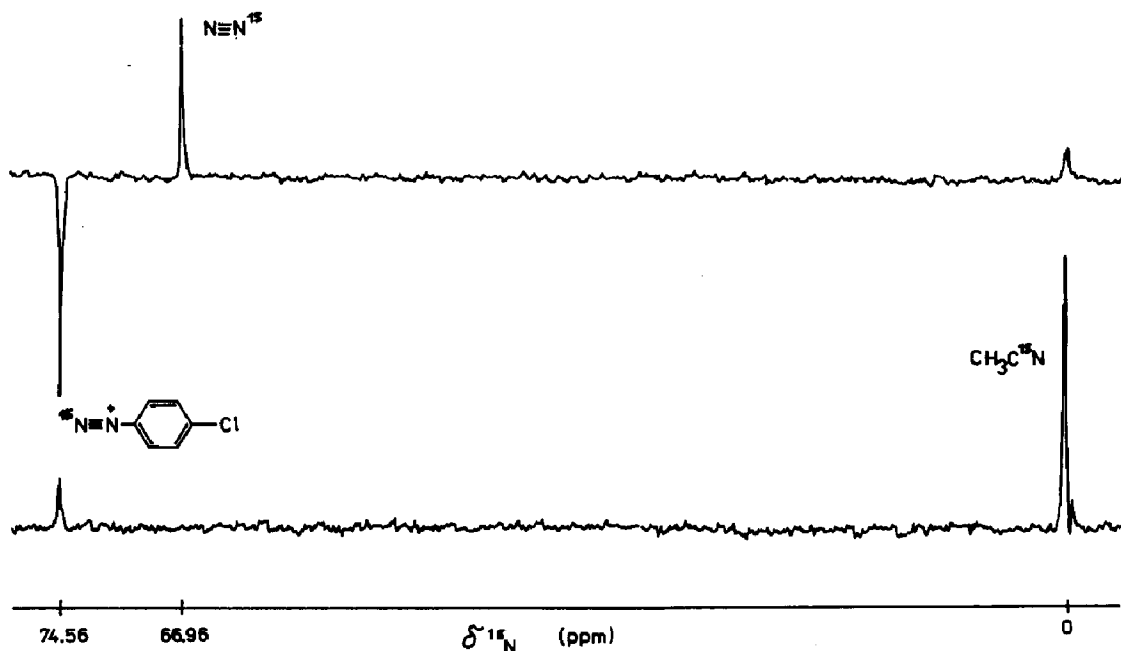
Fig. 2. ^{15}N $\{^1H\}$ photo-CIDNP spectrum at 9.12 MHz of a solution of 0.5 M 4-chloro-benzene diazonium-β-^{15}N tetrafluoroborate and 0.1 M benzophenone in acetonitrile-d_3: upper curve, $\lambda_{exc} > 300$ nm; lower curve, normal nuclear magnetic resonance spectrum of the system. 25 scans were taken for each curve.

TABLE 2

^{13}C and ^{15}N photo-CIDNP effects observed during the photolysis of 0.5 M 4-chloro-benzene diazonium tetrafluoroborate and 0.5 M 4-cyanobenzene diazonium-β-^{15}N tetra-fluoroborate in the presence of aromatic ketones and pyrene

Sensitizer[a]	^{13}C CIDNP of $4\text{-}Cl\text{-}C_6H_4N_2^+BF_4^-$ at C1 [b, c]	^{15}N-CIDNP of $4\text{-}CN\text{—}C_6H_4\overset{+}{N}\equiv^{15}NBF_4^-$ [b, d]		Precursor multiplicity
		$Ar\text{—}\overset{+}{N}\equiv^{15}N$	$^{15}N\equiv N$	
BP	E	E	A	Triplet
X	E	E	A	Triplet
TX	E	E	A	Triplet
F	Not studied	A	E	Singlet
Bz	Not studied	E	A	Triplet
DMBP	E	E	A	Triplet
Py	A	A	E	Singlet

Only the sensitizer was excited (wavelength more than 320 nm).
[a] Sensitizer concentration, 0.1 M.
[b] A, enhanced absorption; E, emission.
[c] In acetonitrile-d_3. Owing to signal broadening no CIDNP signal from the escape product 4-chlorobenzene-d was detected. In the presence of small quantities of trichloromethane the CIDNP signal (E) of the escape product chlorobenzene was observed.
[d] In acetonitrile.

may be found which have different patterns from those produced by the more common radical-pair mechanism.

The normal mechanism for the electron-transfer dediazoniation of arene diazonium salts is well documented [23]:

$$Ar\overset{+}{-}N\equiv N + (e^-) \longrightarrow Ar-N=N\cdot \longrightarrow N_2 + Ar\cdot \xrightarrow{R-H} Ar-H \tag{1}$$
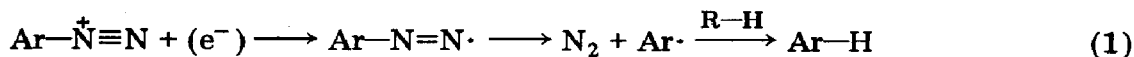
The occurrence of photo-CIDNP signals characteristic of both the cage and escape products can be taken as evidence that aromatic ketones sensitize the dediazoniation of arene diazonium salts by electron transfer according to the following mechanism:

$$\tag{I}$$
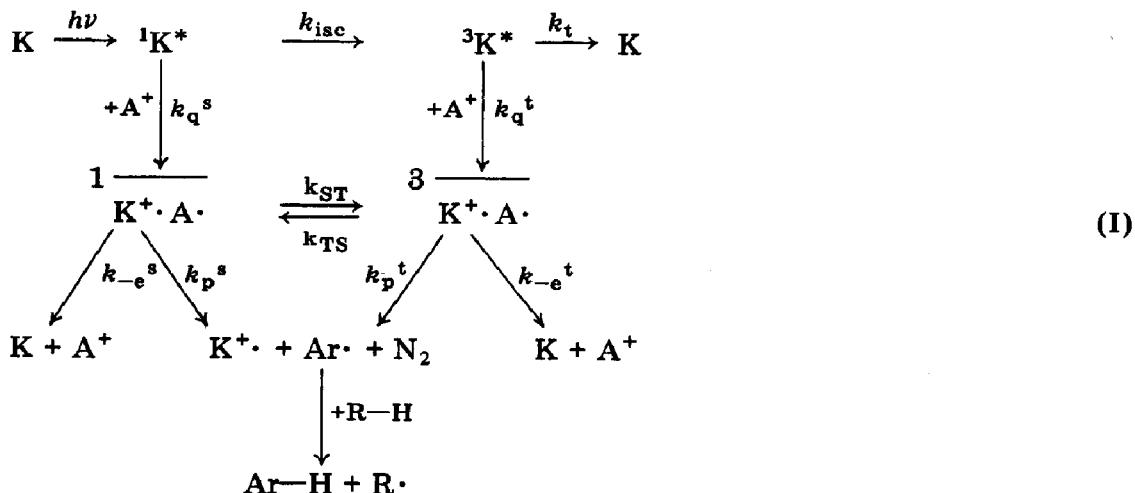
where K represents a ketone, A^+ represents $Ar\overset{+}{-}N\equiv N$ and $A\cdot$ represents $Ar-N=N\cdot$.

The existence of the aryldiazo radicals $Ar-N=N\cdot$ has been demonstrated by electron paramagnetic resonance spectroscopy [24] and pulse radiolysis [25]. According to ref. 25 the rate constants of the monomolecular dediazoniation of $Ar-N=N\cdot$ are in the range from 10^5 s^{-1} (p-NMe$_2$) to 10^7 s^{-1} (p-CN). Thus the homogeneous recombination of the out-of-cage radical pairs $K^+\cdot + A\cdot$, which is not explicitly included in the above scheme, need not be taken into consideration; this second-order reaction cannot compete with the first-order dediazoniation because of the low concentration of radicals during photolysis.

It can be seen from Figs. 1 and 2 and Table 2 that, except for fluorenone and the singlet sensitizer pyrene, all the CIDNP spectra show emission signals for the re-formed diazonium salt (cage product) and enhanced absorption for $^{15}N\equiv N$ (escape product). Comparison with the signs of the CIDNP effects in the presence of pyrene [3, 14] shows that triplet precursors are responsible for the CIDNP spectra of all ketones except fluorenone.

The signs of the CIDNP effects observed are correctly predicted by the extended Kaptein rule [26]

$$\Gamma = \mu\epsilon \, \Delta g \, a_i \, \text{sgn} \, \gamma \, f_{ec} \tag{2}$$

In the case of the $^{13}C(1)$ (cage product) CIDNP effect we obtain

$$\Gamma_{^{13}C} = \mu(+)(-)(+)(+)(+)$$

where $\mu = (-)$ for the singlet reaction (enhanced absorption) and $\mu = (+)$ for the triplet reaction (emission). In the case of the ^{15}N CIDNP effect for the re-formed diazonium salt (cage product) we obtain

$$\Gamma_{^{15}N} = \mu(+)(-)(-)(-)(+)$$

where $\mu = (-)$ for the singlet reaction (enhanced absorption) and $\mu = (+)$ for the triplet reaction (emission). The signs of the effects for the escape product $^{15}N{\equiv}N$ must be reversed because $\epsilon = (-)$.

The value of Δg poses a problem in solving eqn. (2) because only the g factor of the benzophenone cation radical is known ($g_{Ph_2CO^+} = 2.0033 \pm 0.0002$). However, it can be assumed that the other ketones studied in this work have g factors of a similar order, and since $g_{PhN=N^+} = 2.0006$ is very low a negative value for Δg can safely be assumed in all cases. The factors $a_{^{13}C(1)}$ and $a_{^{15}N}$ are positive and negative respectively. The exit channel factor f_{ec} is positive in all cases because the lowest triplet states of the electron donors (ketones) have higher energies than the corresponding radical pairs ($\Delta E \approx 0.6$ - 2.0 eV). The triplet energies of the diazonium salts are probably even higher than those of the ketones (see below).

CIDNP signals from the re-formed ketones (cage products) were not detected. Their absence may be due to exchange between the cation radicals and the ground state ketones.

Further evidence for the conclusion that we are dealing with electron transfer reactions is provided by the observation that benzene, which is the product of a free-radical mechanism, is formed almost exclusively. If energy transfer were taking place we would expect to obtain substitution products (phenol in the presence of water) via the phenyl cation as predicted by symmetry considerations [5].

The observation of CIDNP signals for fluorenone which do not indicate a triplet reaction are now discussed. High concentrations of diazonium salts (about 0.5 M) are used in the photo-CIDNP experiments. Thus the singlet excited state of the ketones may be trapped by the diazonium salt unless the intersystem crossing (ISC) rate constants are so high that the bimolecular quenching reaction cannot efficiently compete with the monomolecular ISC. Values of the ISC quantum yields, fluorescence lifetimes $\tau_0{}^s$ and fluorescence quenching constants $k_q{}^s$ are included in Table 1. Since the ISC quantum yields of the ketones investigated approach unity, $1/\tau_0{}^s$ can be taken as k_{ISC}. In contrast, the singlet quenching rate constants are nearly diffusion controlled. Thus the rates of fluorescence quenching under the conditions of the photo-CIDNP experiments ($[ArN_2^+] \approx 0.3$ M) are $k' = k_q{}^s[ArN_2^+] \approx 10^9 - 10^8$ s^{-1}, and in all cases except fluorenone k_{ISC} competes with singlet quenching sufficiently for the development of (triplet) CIDNP effects. Fluorenone has

a low k_{ISC}^0 of 5.5×10^7 s^{-1} (from τ_0^s and ϕ_{ISC}^0) and is therefore already quenched in its singlet excited state by the diazonium salt which leads to CIDNP effects with the same sign as those obtained with pyrene ($k_{ISC}^0 = 2 \times 10^6$ s^{-1}).

The condition for efficient energy transfer is that an energetically low-lying excited triplet state ($-\Delta G_{ET} \gtrsim 10$ kJ mol^{-1}) exists in the acceptor. According to quantum-mechanical calculations [6] the (relaxed) triplet state of the benzene diazonium salt has an energy of about 4 eV, which is in agreement with the observations of Kikuchi and coworkers [27] who found a phosphorescence band corresponding to a triplet energy of 3.35 eV for benzene diazonium tetrafluoroborate in ethanol at 77 K. Other workers [28] have found phosphorescence bands for p-bromobenzene diazonium salt ($E_T = 2.48$ eV) and p-methoxybenzene diazonium salt ($E_T = 2.73$ eV) in ethanol–methanol mixtures at 4.2 K. These data enable us to estimate the E_T value of the benzene diazonium salt as about 2.6 eV. If this value were correct, the CIDNP exit channel factor for benzil would be different from those for benzophenone, xanthone, thioxanthone and DMBP, which is clearly not the case. Furthermore the phosphorescence results have recently been questioned [29]. In conclusion, energy transfer from triplet excited ketones to arene diazonium salts seems improbable.

In fact electron transfer from triplet excited ketones to arene diazonium salts is thermodynamically possible since in all cases (see Table 1) a negative free energy is obtained from the relationship

$$^3\Delta G_e^\circ = E_{1/2}^{ox}(\text{ketone}) - E_{1/2}^{red}(ArN_2^+) - E_T(\text{ketone}) \tag{3}$$

(Since no radical ion pairs are formed but only a positive charge is transferred from the diazonium salt to the ketone, it is not necessary to include a Coulomb term.)

The oxidation potentials of the ketones can be estimated from the (vertical) ionization energies by means of the Pysh–Yang equation [30]

$$E_{1/2}^{ox} = 0.68IE - 3.95 \tag{4}$$

The applicability of this equation has been proved for acetophenone and thioxanthone where both the vertical ionization energies and the oxidation half-wave potentials are known.

Since the $^3\Delta G_e^\circ$ values are negative, the rate constants for triplet ketone quenching must reach the diffusion-controlled limit. Our value of k_q^t for benzil as determined by phosphorescence quenching is much higher than that reported by Scaiano and Kim-Thuan [8]; the reason for this discrepancy is not clear.

It may seem unusual for ketones to act as reductants, but in fact their ionization potentials are lower than those of alcohols. It has been shown that triplet excited duroquinone is reduced by acetone as is shown by the spectroscopic detection of the acetone cation radical ($\lambda_{max} = 600$ nm) [31]. In the present work transients at 720 nm and 520 nm were observed during the flash photolysis of the xanthone–4-methoxybenzene diazonium tetrafluoro-

borate and xanthone–4-chlorobenzene diazonium tetrafluoroborate systems respectively; these may correspond to the ketone cation radicals. It should also be noted that Pappas *et al.* [32] have postulated electron transfer from triplet excited ketones to diphenyl iodonium salts, but they did not give any experimental evidence for this.

The kinetic model

$$\Phi_p = \phi_{abs}\eta_e{}^s\eta_p{}^s + \phi_{ISC}\eta_e{}^t\eta_p{}^t$$

$$= S\eta_p{}^s + T\eta_p{}^t \tag{5a}$$

$$\Phi_p = \frac{k_e{}^s[A]}{k_e{}^s[A] + 1/\tau_0{}^s}\eta_p{}^s + \frac{\phi_{ISC}{}^0 k_e{}^t[A]}{(k_e{}^s[A] + 1/\tau_0{}^s)(k_e{}^t[A] + 1/\tau_0{}^t)}\eta_p{}^t \tag{5b}$$

where $\phi_{abs} = 1$ and

$$\phi_{ISC} = \frac{\phi_{ISC}{}^0}{\tau_0{}^s k_e{}^s[A] + 1} \tag{5c}$$

can be derived from scheme (I) (k_{ST}/k_{TS} was neglected). The values of $\tau_0{}^s$, $\tau_0{}^t$, $k_q{}^s$ and $k_q{}^t$ given in Table 1 (the k_q values are used for k_e) were used to calculate the factors S and T in eqn. (5) for $[\mathrm{PhN_2^+BF_4^-}] = 10^{-2}$ M. The results, which are given in Table 3, show the following: electron transfer from benzophenone, xanthone and probably DMBP to benzene diazonium tetrafluoroborate is exclusively from the excited triplet states; electron transfer from thioxanthone is predominantly from the excited triplet state; electron transfer from fluorenone is predominantly from the excited singlet state; electron transfer from pyrene is exclusively from the excited singlet state. This is in agreement with the CIDNP results (see Table 1).

TABLE 3

Participation of singlet S and triplet T pathways in the overall quantum yields according to eqn. (5) and the k_{-e}/k_p values according to eqn. (5)

Ketone	$\phi_{ISC}{}^0$	ϕ_{ISC}[a]	S	T	k_{-e}/k_p	k_q values used [b] ($\mathrm{M^{-1}\,s^{-1}}$)
BP	1.0	0.993	0.0007	0.993	1.70	$k_q{}^t = 8.5 \times 10^9$
X	1.0[c]	0.993	0.0007	0.993	2.03	$k_q{}^t = 8.5 \times 10^9$
TX[d]	1.0	0.678	0.322	0.677	6.53	$k_q{}^s = 9.8 \times 10^9$
F	0.93	0.374	0.594	0.374	17.7	$k_q{}^s = 3.8 \times 10^9$
Bz	0.92	0.786	0.145	0.785	8.83	
Py	0.38	0.0003	0.993	0.0003	1.63[e]	

$[\mathrm{PhN_2^+BF_4^-}] = 10^{-2}$ M.
[a] According to eqn. (5c).
[b] Estimated according to the $\Delta G_e{}^\circ$ criterion.
[c] Estimated.
[d] Calculated using $\tau_0{}^s = 5600$ ps.
[e] Calculated for the singlet reaction ($S = 1$, $T = 0$).

The product quantum yields are roughly proportional to ϕ_{ISC} (eqn. 5c). If it is assumed that only the triplet electron transfer leads to effective dediazoniation[†], the ratio k_{-e}/k_p can be calculated using eqn. (5) (see Table 3):

$$\frac{T}{\Phi_p} = \frac{1}{\eta_p{}^t} = \frac{k_p{}^t + k_{-e}{}^t}{k_p{}^t} = 1 + \frac{k_{-e}{}^t}{k_p{}^t} \tag{6}$$

where $k_p{}^t$ represents essentially the rate constant of the escape of the radicals from the cage. As discussed earlier the recombination of homogeneous radical pairs does not play a role.

It is surprising that the values of k_{-e}/k_p (or Φ_p) for the triplet electron donors and Py are similar because the geminate back electron transfer in the singlet radical pair formed on electron transfer from singlet excited Py to benzene diazonium salt is symmetry allowed and is therefore expected to proceed very fast, giving higher k_{-e}/k_p values than those of the triplet systems. If an exciplex is formed before the geminate radical pair, so that an additional deactivation channel is available, quantum yields of less than unity can be explained, but the symmetry rules for the back electron transfer should remain valid. It seems that effective singlet–triplet mixing operates in the low magnetic field (earth's magnetic field) present in this case which, according to the theory of magnetic effects, can only be a spin flip mechanism (nuclear Overhauser effect). This does not seem improbable because ^{14}N has a nuclear spin moment I of unity and a rather large hyperfine interaction constant ($a_{^{14}N} \approx 2.0$ mT) in the aryldiazo radicals. In fact CIDNP experiments at low fields (about 1.5 mT) support this explanation. This will be discussed elsewhere.

Arylphosphonium and diaryliodonium compounds are also cleaved on sensitization by photoexcited ketones and in these cases an electron transfer mechanism has to be assumed. This will be discussed elsewhere.

Acknowledgment

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