Laser flash photolysis of dinaphthyl ketones

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Abstract

The photophysics and photochemistry of 1,1'-, 1,2'-, and 2,2'-dinaphthyl ketones and a related 2,3,5,6-dibenzofluorenone were studied by laser flash photolysis techniques in organic solvents. Their photochemistry is dominated by the triplet state, which has a π,π^* character. This is consistent with their phosphorescence spectra, as is the high efficiency of the sensitization of singlet oxygen generation, $\Phi = 0.9$–0.96 in acetonitrile. Self-quenching plays an important role in determining triplet lifetimes in solution. The dinaphthyl ketone triplets are not photoreduced by 2-propanol, a common hydrogen donor toward n,π^* ketone triplets. The energies of dinaphthyl ketone triplets range from $E_T = 53.8$ for rigid 2,3,5,6-dibenzofluorenone to 59.2 kcal mol^{-1} for flexible 2,2'-dinaphthyl ketone, and reflect the degree of conjugation of the carbonyl group and naphthalene rings promoted by their ability to approach a coplanar conformation. The reactions of the dinaphthyl ketone triplets with 1,4-diazabicyclo[2.2.2]octane (DABCO), triethylamine, 1,4-cyclohexadiene and 2,4,6-trimethylphenol indicate their strong preference for electron transfer. For example, the electron transfer from DABCO to 2,3,5,6-dibenzofluorenone triplet in methanol occurs with $k = 9.9 \times 10^8$ M^{-1} s^{-1}, and is almost two orders of magnitude faster than H-atom abstraction from an excellent H-atom donor 1,4-cyclohexadiene ($k = 1.4 \times 10^7$ M^{-1} s^{-1}). Hydrogen bonding between the reactants plays a major role in the reactions with 2,4,6-trimethylphenol. The reactivities in non-hydrogen bonding hexane, are considerably higher than in methanol, where the hydrogen bonds with the solvent hinder the interaction between the reactants. © 1997 Elsevier Science S.A.

Keywords: Laser photolysis; Carbonyl compounds; Self-quenching; Energy transfer; Hydrogen transfer

1. Introduction

We have used emission spectroscopy and laser flash photolysis techniques to characterize the triplet states of dinaphthyl ketones and their bridged analogue, dibenzofluorenone. The π,π^* character of the dinaphthyl ketones and dibenzofluorenone triplets is unambiguously determined, as expected for these electron-rich, highly delocalized aromatic molecules, whose spectral properties are dominated by the naphthalene chromophore. The dynamics for the photoreduction of the triplets by triethylamine, 2,4,6-trimethylphenol and 1,4-cyclohexadiene was investigated in three classes of solvent, nonpolar hexane, polar acetonitrile, and protic methanol. Electron transfer from triethylamine in polar solvents yields radical anions, clearly different from the radicals that result from reaction with 1,4-cyclohexadiene in non polar media.

2. Materials and methods

1,1'-Dinaphthyl ketone (1,1'-DNK) was synthesized from 1-naphthyl magnesium bromide and 2 moles of 1-naphthoyl chloride in ether as described previously [1]. After recrystallization from ether the sample had m.p. 104–105 °C (Ref. [1] 104–105 °C).

2,2'-Dinaphthyl ketone (2,2'-DNK) was synthesized from 2-naphthoyl magnesium bromide and 2-naphthoyl chloride in ether in accord with literature protocol [2]. The ketone was recrystallized from 1-chlorobutane to give crystals m.p. 164–165 °C (Ref. [2] 163 °C, Ref. [3] 159–161 °C, Ref. [4] 165 °C).

1,2'-Dinaphthyl ketone (1,2'-DNK) was synthesized from 1-naphthyl magnesium bromide and 2-naphthoyl chloride following the method of Blicke [1]. The sample was recrystallized from ethanol to give crystals m.p. 135–136 °C (Ref. [4] 136–137 °C, Ref. [5] 135 °C). 2,3,6,7-Dibenzofluorenone (DBF) was synthesized according to the method of Cook and Preston [6].

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1,1'-DNK   1,2'-DNK

2,2'-DNK   DBF
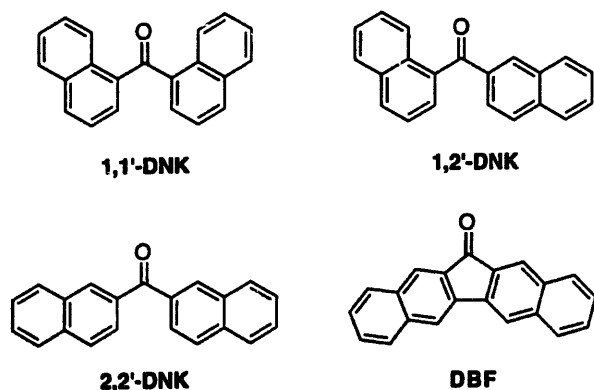
All other chemicals used in this study were commercially available and were used without further purification. Triethylamine, 1,4-cyclohexadiene, 2,4,6-trimethylphenol, 1,4-diazabicyclo[2.2.2]octane (DABCO), and phenazine were Aldrich products. The solvents, acetonitrile, methanol and hexane, were Omnisolv grade from BDH. Water was purified through a Millipore Milli Q system to a resistivity better than 18 MΩ cm^{-1}. The concentration of oxygen was adjusted by bubbling the samples with high purity gases, N_2 and O_2, from Matheson.

Phosphorescence spectra were recorded in 2-propanol: methanol (9:1) glasses at 77°K using the Perkin Elmer LS 50 luminescence spectrometer.

Lumonics EX-530 excimer (Xe/HCl/He, 308 nm, ~6 ns, 60–120 mJ/pulse) or the third harmonic from a Continuum Surelite Nd-YAG (355 nm, ~6 ns, ~20 mJ/pulse) lasers were used for sample excitation. The data acquisition and processing were handled by a Tektronix 2440 digital oscilloscope interfaced to a PowerMacintosh computer operating with custom software developed in the LabVIEW 3.1.1 environment from the National Instruments. The sample solutions were irradiated in 7×7 mm^2 Suprasil quartz cells with 90° excitation. To avoid errors due to the accumulation of products, the samples were often irradiated in a flow cell attached to a reservoir where the stock solution was deaerated.

Singlet oxygen yields were measured using the time resolved infrared emission instrumentation described previously [7]. The solutions of dinaphthylketones in acetonitrile were saturated with oxygen and excited with laser pulses at 355 nm. The emission signals (1270 nm) were monitored with a germanium photodiode detector and amplified with a Stanford Research Systems low noise preamplifier (model SR560). The rest of the system was the same utilized for the laser flash photolysis experiments. In order to determine the quantum yields of singlet oxygen formation, exactly optically matched phenazine and 4,4'-dimethoxybenzophenone solutions (for which the efficiency of singlet oxygen generation is well established) were used as Ref. [8]. The laser dose was varied from 0–27 mJ/pulse, and the quantum yields were derived from the slopes of linear signal vs. dose plots.

3. Results and discussion

The phosphorescence spectra of the ketones were determined in a 2-propanol–methanol (9:1) glass at 77 K. These spectra show good vibrational resolution, comparable with that observed in the case of naphthalene. Table 1 gives the triplet energies determined from the 0,0 phosphorescence bands. For comparison, data have been also included for benzophenone and naphthalene.

It is clear from Table 1 that the excited triplet states of the dinaphthyl ketones have π,π^* character. The energies are substantially lower than that of the n,π^* triplet of benzophenone, but in line with values expected for substituted naphthalenes [9,10]. Clearly the dominant spectroscopic features are those of the lowest energy chromophore in the system, i.e. the naphthyl moiety.

The energy of the 2,2'-dinaphthyl ketone (2,2'-DNK) triplet is higher than those of other substituted dinaphthyl ketones, probably as a result of the unrestricted rotation of the naphthalene rings about the axis of C–C(=O)–C bonds. The consequence of freely rotating naphthalene rings is somewhat lower degree of delocalization of the unpaired electron leading to slightly more 'aliphatic' character of the carbonyl group. In addition, because of electron density distribution within the naphthalene rings, the unpaired electron is less delocalized at the C2 positions.

The π,π^* character of the dinaphthyl ketones and dibenzofluorenone triplets is also evident from their lack of reactivity toward 2-propanol. Thus, $k < 10^5$ M^{-1} s^{-1} was estimated in neat 2-propanol, because the decay of the dinaphthyl ketone triplets was unchanged as compared with methanol. For comparison, a typical n,π^* triplet, such as that of benzophenone, reacts with 2-propanol with a rate constant of ~10^6 M^{-1} s^{-1} [11]. In addition, energy transfer to oxygen is very efficient, with ϕ ~1.0 (see Table 2), which is common with the aromatic π,π^* triplets [12], but too high for a n,π^* ketone triplet. Based on recent work from our laboratory [13], the expected efficiency for an n,π^* triplet would be ca. 0.41 for a triplet energy of 58 kcal/mol. The quantum yield of singlet oxygen from quenching of the dibenzofluorenone triplet is somewhat lower, $\Phi = 0.65$ (Table 2).

Table 1
Triplet energies for dinaphthyl ketones and related compounds determined from 77 k phosphorescence spectra in alcohol glass

Triplet, from	$\Delta E(T_1 \rightarrow S_0)_m$, kcal mol^{-1}
1,1'-Dinaphthyl ketone	56.5
1,2'-Dinaphthyl ketone	57.8
2,2'-Dinaphthyl ketone	59.2
Dibenzofluorenone	53.8
Naphthalene	60.9 [a]
Benzophenone	69.2 [a]

[a] From [25] for a polar solvent.

Table 2

Quenching of dinaphthyl ketone triplets by oxygen in acetonitrile, measured by laser flash photolysis at 20 °C

Triplet from	ϕ/ϕ(Phenazine) [a]	ϕ/ϕ(4,4'-Dimethoxy-benzophenone) [a]	$\phi(^1\Delta_g O_2)$ [b]
1,1'-DNK	1.15	2.25	0.93
1,2'-DNK	1.12	2.18	0.90
2,2'-DNK	1.20	2.34	0.97
DBF	0.8	1.57	0.65

[a] Quantum yield of singlet oxygen from quenching of phenazine, ϕ_Δ =0.83, and 4,4'-dimethoxybenzophenone, ϕ_Δ = 0.40, are taken as standards [8].
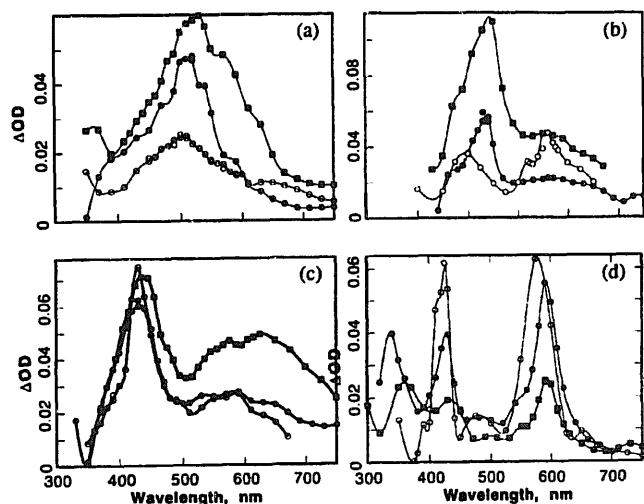[b] Calculated as the arithmetic mean of the measured values. Estimated to be accurate to ± 15%.

Fig. 1. Absorption spectra of the dinaphthyl ketone triplets measured by laser flash photolysis in N_2-saturated organic solutions (–●– acetonitrile, –■– methanol and –O– hexane) of ~ 50 μM dinaphthyl ketone at 20 °C, upon 308 nm laser pulse. (A) 1,1'-DNK; (B) 1,2'-DNK; (C) 2,2'-DNK; and (D) DBF.

3.1. Characteristics of dinaphthyl ketone triplets; spectra and lifetimes

The triplet–triplet absorption spectra of the ketone under study were recorded in solvents of various polarities, and the results are presented in Fig. 1.

There is a slight bathochromic shift, ~ 20 nm for the long wavelength and ~ 10 nm for the short wavelength band, in nonpolar hexane as compared with acetonitrile, again a characteristic of the π,π^* triplets. The spectrum of the 1,1'-DNK triplet has a broad band centered around 500 nm, while the spectra of the 1,2'- and 2,2'-DNK triplets feature two bands, a weaker broad absorption around 600 nm and a stronger band around 420 nm; the latter is reminiscent of the absorption from triplet naphthalene.

The lifetimes of the 1,1'- and 1,2'-DNK and dibenzofluorenone (DBF) triplets are quite long in all solvents, e.g. τ~ 10 μs in acetonitrile. These lifetimes seem to be largely controlled by self-quenching, a rather common process in long lived triplet ketones [14]. Thus, the triplet lifetimes are clearly concentration dependent. The decay data from indi-
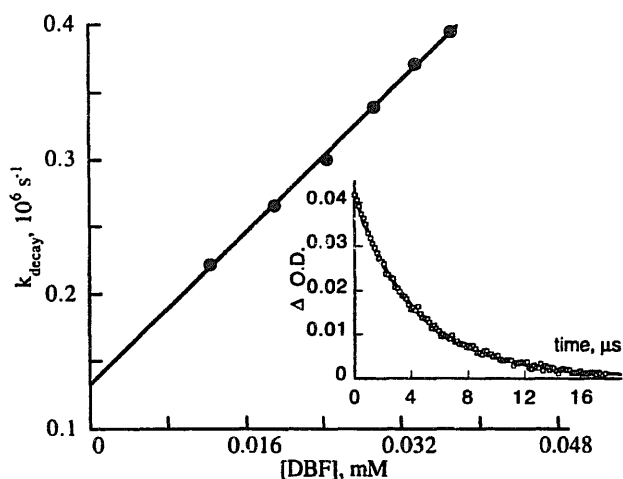

Fig. 2. Dependence of the first order component of the decay of DBF triplet upon the concentration of precursor. Excitation at 308 nm, monitored at 590 nm. Inset: Decay trace for 0.0123 mM DBF; the fit indicates approximately equal contributions from first and second order decays. The former predominates at the higher DBF concentrations.

Table 3

Self-quenching data for dinaphthyl ketones in acetonitrile at room temperature

Triplet from	k_0 (s^{-1})	k_{sq} (M^{-1} s^{-1})
1,1'-DNK	$(1.1 \pm 0.2) \times 10^5$	$(1.1 \pm 0.1) \times 10^9$
1,2'-DNK	$(6.8 \pm 2.0) \times 10^4$	$(2.1 \pm 0.1) \times 10^9$
2,2'-DNK	$(5 \pm 3) \times 10^4$	$(1.7 \pm 0.2) \times 10^9$
DBF	$(1.3 \pm 0.1) \times 10^5$	$(7.1 \pm 0.2) \times 10^9$

vidual traces was fitted with a combination of first and second order kinetics; the latter takes into account the involvement of triplet–triplet annihilation, which is quite common with long lived triplets under conditions of laser excitation. A plot of the first order (or rather pseudo-first order) contribution as a function of the ketone concentration yields k_{sq}, the self-quenching rate constant from the slope. A representative plot is shown in Fig. 2, where the inset illustrates a representative decay trace and the first/second order fit. The data obtained have been summarized in Table 3. The values of k_0 are extrapolated to zero concentration, where no self-quenching can occur. The reciprocal of k_0 is the extrapolated triplet lifetime. As is usual with these very long lifetimes, it is conceivable that even longer values could be obtained by exhaustive solvent purification and/or removal of traces of oxygen. Again, these observations are quite typical for π,π^* triplets.

## 3.2. Photoreduction of dinaphthyl ketone triplets

Photoreduction of the dinaphthyl ketone triplets by DABCO, triethylamine, 1,4-cyclohexadiene and 2,4,6-trimethylphenol has been studied in acetonitrile, methanol and hexane to assess the influence of the hydrogen bonding and polarity of the solvent on the mechanism of reaction. The quenchers selected are DABCO, triethylamine (electron transfer), 1,4-cyclohexadiene (H-donor), and 2,4,6-trime-

thylphenol that could act both as an electron and H-atom donor.

Quite frequently, photoreduction converts any aromatic ketone triplet to the ketyl radical, which may be protonated or ionized, depending on its acid-base equilibrium and the proton donating ability of the solvent [15–21]. One electron transfer from an electron donor generates a radical anion, whereas an H-atom abstraction from a weak X–H bond forms a ketyl radical (neutral). In addition to the dinaphthyl ketone ketyl radical, a quencher-derived radical is also formed, but the radicals of triethylamine (radical cations), and 1,4-cyclohexadiene (allyl radical) do not absorb strongly above 350 nm, where the dinaphthyl ketone radicals are expected to have absorption bands. In the case of DABCO, its radical cation has a weak band in the visible region, although it overlaps extensively with signals derived from the ketones under study, and is not a useful diagnostic tool in this case. The phenoxyl radical from 2,4,6-trimethylphenol has a strong 370 nm band and a weaker band at 600 nm (see Fig. 4 later in the text), similar to the spectra of o-substituted phenoxyl radicals [22]. We note that a number of examples have recently been reported where hydrogen atom abstraction by π,π^* triplet aromatic ketones involves reactivity at the aromatic ring, rather than at the carbonyl group [23,24]. Our results do not address this question, although it should be noted that such a mechanism cannot be ruled out in the case of 1,4-cyclohexadiene.

3.2.1. Electron transfer from amines

Aliphatic amines, such as 1,4-diazabicyclo-[2.2.2]-octane (DABCO) in acetonitrile, with $E_{ox} = 0.68$ V vs. SCE [21], is an excellent electron donor. For example, DABCO rapidly and efficiently quenches n,π^* triplets of benzophenone [15,17,20], and decafluorobenzophenone [21] to form efficiently the corresponding radical anions and DABCO radical cation. The reaction of the dinaphthyl ketones and dibenzofluorenone triplets with DABCO must be an electron transfer, since DABCO has no easily abstractable hydrogens due to unfavorable stereoelectronic effects. The quenching of 2,2'-DNK triplet by DABCO in methanol occurs with a rate constant of $4.5 \pm 0.1 \times 10^7$ M^{-1} s^{-1}.
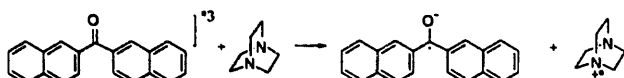
The reaction in methanol is substantially faster than in nonpolar hexane, with $k \leq 1 \times 10^6$ M^{-1} s^{-1}. Similarly, photoreaction of DBF triplet by DABCO is more than three orders of magnitude faster in methanol, $k = 9.9 \pm 0.1 \times 10^9$ M^{-1} s^{-1}, than in nonpolar hexane, $k = 4 \pm 1 \times 10^6$ M^{-1} s^{-1}, thus suggesting an electron transfer process.

The reaction of dinaphthyl ketone and DBF triplets with triethylamine is also an electron transfer reaction, as evidenced from the build up of the ~ 650 nm band of the corresponding radical anions. The band is seen in all solvents used in this study, which means that the mechanism of the

reaction does not depend on either polarity or proton donating ability of the solvent. This is in contrast with the photoreduction of the benzophenone and decafluorobenzophenone triplets [15,17,20,21], where the formation of the ketyl radical from the ion pairs depend on the oxidation potential of amine and the polarity and proton donating ability of the solvent. Furthermore, it is conceivable that the basicity of triethylamine, which is present at ~ 1 M concentrations, contributes appreciably to the stability of dinaphthyl ketone radical anions irrespective of the solvent.

The spectra of dinaphthyl ketone anion radicals generated by the triethylamine-induced photoreduction of corresponding triplets are shown in Fig. 3. The spectra feature two prominent bands, one around 410 nm and the other around 720 nm. Both bands are more intense than the absorption of the triplet state. The reaction rate constants of the photoreduction of dinaphthyl ketone and dibenzofluorenone triplets by triethylamine in various solvents are summarized in Table 4. As may be expected for an electron transfer process, where a polar solvent facilitates charge separation in the transition state, the rate constants are an order of magnitude slower in nonpolar hexane as compared with polar acetonitrile.
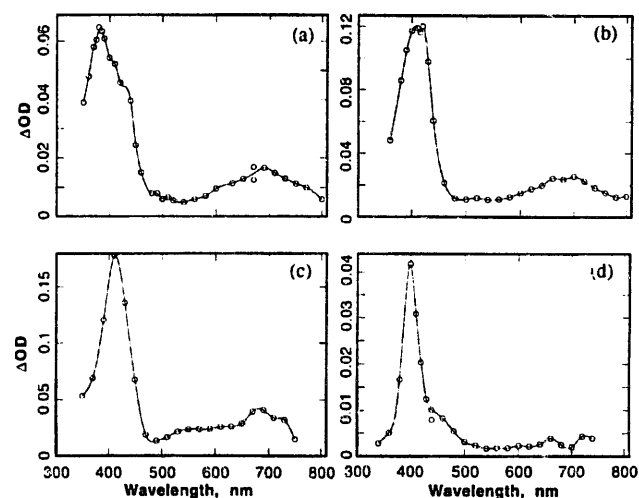

Fig. 3. Absorption spectra of the dinaphthyl ketone anion radicals determined by laser flash photolysis (308 nm laser) upon completion of one electron transfer from triethylamine to the dinaphthyl ketone triplets in N$_2$-saturated acetonitrile solutions of ~ 50 μM dinaphthyl ketone and 1 M triethylamine at 20 °C. (A) 1,1'-DNK; (B) 1,2'-DNK; (C) 2,2'-DNK; and (D) DBF (concentration of triethylamine was 0.1 M).

Table 4
Rate constants for the photoreduction of dinaphthyl ketone triplets with triethylamine in organic solvents determined by laser flash photolysis (308 and 355 nm laser) at 20 °C

k,[a] M^{-1} s^{-1}

Triplet from	Acetonitrile	Hexane	Methanol
1,1'-DNK	1.3×10^7	8.4×10^5	5.6×10^6
1,2'-DNK	1.5×10^7	7.3×10^5	7.0×10^6
2,2'-DNK	1.6×10^7	1.9×10^6	9.0×10^6
DBF	4.6×10^8	1.4×10^7	4.1×10^8

[a] Estimated to be accurate to $\pm 10\%$.

The photoreduction of the 2,2'-dinaphthylketone and dibenzofluorenone triplets by triethylamine has been studied in deuterated methanol (CH_3OD), to further elucidate the mechanism. The deuterium isotope effects are $\frac{k_H}{k_H} = 0.8$ and 1.0 for the 2,2'-dinaphthyl ketone and dibenzofluorenone reaction, respectively. The lack of isotope effect suggests that the mechanism is electron transfer, ruling out any participation of H-transfer in the rate determining step.

3.2.2. H-abstraction from 1,4-cyclohexadiene

The reaction of dinaphthyl ketone triplets by 1,4-cyclohexadiene – a well-known H-atom donor [25] – can lead to the cyclohexadienyl radicals and the ketone-derived ketyl radical.
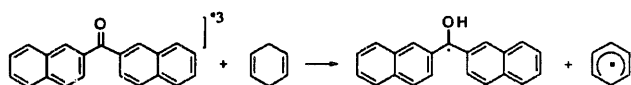
Alternatively, the process may involve some attack at the aromatic rings, as recently reported for other systems, including xanthone [23,24].

The reaction with 1,4-cyclohexadiene is a slow process (Table 5), having in mind that the bond strength of the allylic C–H is only 73 kcal mol^{-1} [26]. Relatively low reactivity in the H-atom abstraction reactions seem to be characteristic of the aromatic π,π^* triplets [27], which are not readily photoreduced in the presence of alcohols [11,27].

3.2.3. Reaction with 2,4,6-trimethylphenol

Phenols are well-known electron and H-atom donors [28–30], which is the basis of their excellent antioxidant properties. There is no sharp distinction between these two mechanisms. One electron transfer is believed to be more probable in polar solvents, whereas the H-atom donation may take over in non polar media [31]. One electron transfer from a phenol to an oxidant generates a phenoxyl radical cation and an oxidant anion, which usually must exchange protons either with a solvent or within themselves. The rate constants of the reactions of dinaphthyl ketone triplets with 2,4,6-trimethylphenol are summarized in Table 6. The transient spectra upon the photoreduction of the dinaphthyl ketone triplets by 2,4,6-trimethylphenol are exemplified in Fig. 4. The spectrum of 2,4,6-trimethylphenoxyl radical generated by tert-butoxyl

Table 5

Rate constants of the reactions of dinaphthyl ketone triplets with 1,4-cyclohexadiene in organic solvents determined by laser photolysis (308 and 355 nm) at 20 °C

k,^{a} M^{-1} s^{-1}

Triplet from	Hexane	Methanol
1,1'-DNK	2.2×10^5	3.3×10^5
1,2'-DNK	3×10^5	4.7×10^5
2,2'-DNK	4×10^5	4.1×10^5
DBF	1.7×10^7	1.4×10^7

^{a} Because of slow reactions, the accuracy is estimated as ±30%.

Table 6

Rate constants of the reactions of dinaphthyl ketone triplets with 2,4,6-trimethylphenol in organic solvents determined by laser photolysis (308 and 355 nm) at 20 °C

k,^{a} M^{-1} s^{-1}

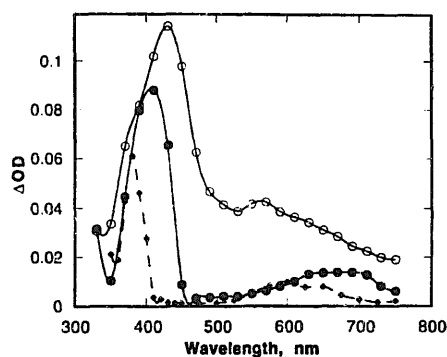| Triplet from	Acetonitrile	Hexane	Methanol
1,1'-DNK	4.8×10^7	2.0×10^9	4.3×10^7
1,2'-DNK	2.0×10^8	4.5×10^9	1.5×10^8
2,2'-DNK	3.4×10^8	5.0×10^9	3.2×10^8
DBF	9.2×10^8	1.05×10^{10}	5.2×10^9

^{a} Estimated to be accurate to ± 10%.

Fig. 4. Absorption spectra of the 1,2'-DNK triplet (–O–) and upon the completion of an electron transfer from 2,4,6-trimethylphenol (–●–) determined by laser flash photolysis (308 nm laser) in an N_2-saturated methanol solution of ~50 μM 1,2'-DNK and 5 mM 2,4,6-trimethyphenol. Broken line- spectrum of the 2,4,6-trimethylphenoxyl radical generated by the tert-butoxyl radical oxidation of phenol (308 nm excitation, 3M di-tert-butyl-peroxide, 9.8 mM 2,4,6-trimethylphenol in N_2-saturated acetonitrile).

radical reaction (from photolysis as di-tert-butyl peroxide [32]) is given for comparison. Clearly, these spectra are composite of those of dinaphthyl ketone and phenoxyl radicals.

It is obvious that the reactions of the dinaphthyl ketone triplets with 2,4,6-trimethylphenol involve the exchange of a hydrogen atom. However, the H-atom abstraction mechanism seems unlikely since the reactions with the phenol are several orders of magnitude faster than with 1,4-cyclohexadiene. While the reactions with the phenol show marked solvent effect (see Table 6), the ratio between two given solvents (e.g. hexane and acetonitrile) is very dependent on the ketone used; this seems to rule out the mechanism that Ingold and coworkers [33,34] have shown for alkoxyl radicals, where solvent effects are determined simply by the fractions of hydrogen bonded and free phenol. The deuterium isotope effect (k_H/k_D) is 1.16 and 2.00 in the reactions of DBF and 2,2'-DNK, respectively. Secondary isotope effects of similar magnitude were previously reported for the electron transfer reactions of peroxyl radicals with organic reductants [31], although small isotope effects are not uncommon in the case of fast reactions.

One-electron reduction of the dinaphthyl ketone triplets requires that an unstable phenoxyl radical cation is generated in addition to a ketyl radical anion. Provided that the proton

exchange between the product radicals occurs in the rate determining step, the degree of hydrogen bonding between the reactants would critically influence the course of the reaction. Similar conclusions about the importance of hydrogen bonding have been reported previously [31,35]. Hydrogen bonding between the phenolic O–H and the carbonyl group apparently plays a crucial role in the reaction, as suggested by Leigh et al. in a recent communication [36]. It is quite possible that under certain conditions proton transfer is the driving force behind hydrogen atom transfer.

4. Conclusions

The photochemistry of dinaphthyl ketones is dominated by their π,π^* triplets. These triplets generate singlet oxygen rapidly and efficiently upon oxygen quenching. The dinaphthyl ketone triplets are efficiently photoreduced by electron donors. They are poor H-atom abstractors, and $k = \sim 4 \times 10^5$ $M^{-1}\,s^{-1}$ with such an excellent H-atom donor as 1,4-cyclohexadiene. The solvent effects emphasize the importance of the hydrogen bonding between the reactants. The ability of 2,4,6-trimethylphenol to form a hydrogen bond with a dinaphthyl ketone appears to control the kinetics of this fast process. For example, one-electron transfer from DABCO ($E_{ox} = 0.68$ V vs. SCE [37] in acetonitrile), without a possibility for hydrogen bonding between the reactants, proceeds at $k(2,2'\text{-DNK}^{*3}+\text{DABCO}) < 10^6$ $M^{-1}\,s^{-1}$ in hexane, whereas the corresponding rate for the hydrogen bonded phenol ($E_{ox} \sim 0.23$ V vs. SCE [38] in acetonitrile) is $k = 1.05 \times 10^{10}\,M^{-1}\,s^{-1}$.

Acknowledgements

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