

Radical species derived from phenalenone: characterization and role of upper excited states[☆]

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Abstract

The reactivity of triplet phenalenone (PN) towards typical H- and electron-donors is characterized by means of nanosecond laser flash-photolysis. H-abstraction from tributylstannane occurs with a rate constant of ca. $5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. From the activation energy for this reaction, an upper limit for the T_2-T_1 energy gap is calculated as $9 \pm 1 \text{ kJ mol}^{-1}$ in nonpolar solvents, consistent with the solvent-insensitive high Φ_T value in phenalenone. Triplet phenalenone also reacts via photoinduced electron transfer with 1,4-diazabicyclo[2.2.2]octane (DABCO) with rate constant close to the diffusional control limit. The spectrum of the solvated free radical anion of phenalenone has a maximum at 440 nm in acetonitrile.

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1. Introduction

Phenalenone (also called perinaphthenone, PN, Fig. 1) is a universal reference for sensitization of singlet oxygen, $\text{O}_2(\text{a}^1\Delta_{\text{g}})$, widely used in photochemistry and photobiology. It is soluble in a large variety of solvents and its quantum yield for singlet oxygen production, Φ_{Δ} , is close to unity in most solvents investigated so far ranging from water to cyclohexane [1–3].

PN is present in the environment as atmospheric and water pollutant [4,5], and some plants produce secondary metabolites containing its skeleton [6–10]. Its photodynamic activity and that of its derivatives has been demonstrated [5,11], and it has recently been used as standard for singlet oxygen-mediated damage to DNA [12,13]. Despite the fact that PN is an extremely good singlet oxygen photosensitizer, its small size and planarity suggests that it might bind to biomolecules, e.g. DNA, whereby direct photoreaction between excited PN and the substrate could take place. PN is able to abstract hydrogen from deoxygenated alcoholic solvents [14–16], although with a quantum yield of only ca. 0.05 [17]. On the other hand, PN is also able to participate in photoinduced electron transfer reactions [14]. Despite these reports on PN's photochemistry, little information is known

about the intermediate species involved. Furthermore, the lowest triplet state of PN is $\pi\pi^*$ character in polar and non-polar solvents [1,18], which is generally considered to be far less reactive than an $n\pi^*$ state towards H-abstraction [19]. Thus, it appears of interest to characterize the radical species produced in such reactions and to examine in greater detail the reactivity of photoexcited PN towards typical H- and electron-donors. Herein, we present the results of a laser flash-photolysis study on the ability of triplet PN to react via H-abstraction or photoinduced electron transfer to yield the ketyl radical and the radical anion, respectively.

2. Experimental

PN, tributylstannane (Bu_3SnH) and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from Aldrich, and the former was recrystallized from methanol. Solvents were from SDS (spectrosol quality) and used as received, except for acetonitrile, which was dried with 3 Å molecular sieves. Transient absorption experiments in the UV-Vis region were carried out using a home-built apparatus. In this instrument, the third harmonic of a pulsed Continuum Surelite Nd:YAG laser was used to irradiate the sample ($\lambda = 355 \text{ nm}$, 5 ns pulsewidth, 1–5 mJ per pulse, 8 mm beam diameter). The absorbance changes were probed at right angles by a CW Xe lamp (PTI, 75 W) and a Hamamatsu R928 photomultiplier. Spectral discrimination was obtained placing a PTI

[☆] Dedicated to the memory of Santi Nonell i Renom (1921–2003).

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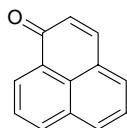


Fig. 1. Molecular structure of PN.

101 monochromator between sample and detector. The detector output was fed to a Lecroy 9410 digital oscilloscope, and acquired by a PC computer for storage and analysis. Temperature in the cuvette was regulated by a circulating water bath. Ground-state UV-Vis absorption spectra were recorded using a Varian Cary 4E spectrophotometer.

3. Results and discussion

Laser irradiation of PN in oxygen-free benzene yields monoexponentially-decaying transients of lifetime ca. 40 μs , which are quenched when air is let into the system. This lifetime is close to that previously reported for ^3PN ($38 \pm 3 \mu\text{s}$) and the transient spectrum (Fig. 2) agrees well with the triplet-minus-singlet (T–S) difference absorption spectrum of PN deduced from previously published triplet and ground-state absorption spectra [1]. We thus, assign the transient in Fig. 2 to the triplet state of PN.

Photoexcitation of PN in 2-propanol solutions yields biexponentially-decaying transients (Fig. 3). The shorter-lived component has a lifetime of $40 \pm 5 \mu\text{s}$ and its spectrum matches the T–S spectrum in Fig. 2. The longer-lived component has a lifetime exceeding the time window of our set-up (ca. 5 ms), and its spectrum shows bleaching and absorption bands in regions where the triplet PN shows the opposite behavior, i.e. at 395 and 425 nm, respectively (Fig. 3, insets). Due to the H-donating ability of the solvent, we assign these new bands to the ketyl radical of PN. This spectrum is consistent with that measured by conventional steady state spectrophotometry in ethanol immediately after laser irradiation, which showed a maximum at around

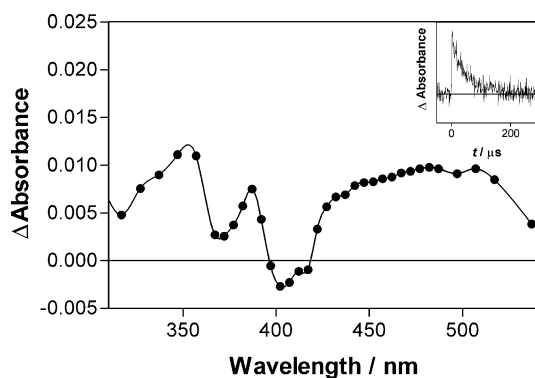


Fig. 2. Transient difference absorption spectrum of PN ($60 \mu\text{M}$) in argon-saturated benzene, immediately after the laser pulse. *Inset*: signal at 350 nm.

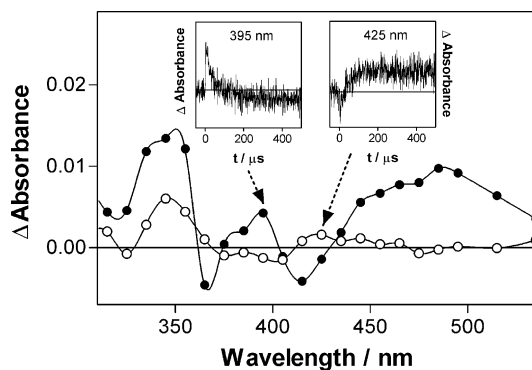


Fig. 3. Transient difference absorption spectra of PN ($60 \mu\text{M}$) in 2-propanol after 3 μs (●) and 200 μs (○). *Insets*: signals at 395 and 425 nm. At 395 nm the triplet shows positive absorption while the persistent ketyl radical shows bleaching. At 425 nm the situation is reversed.

350 nm [17]. A similar behavior is found in water and in toluene, although the ketyl radical is formed to a lesser extent in these solvents.

In order to kinetically characterize the H-abstraction reaction, Bu_3SnH , a very efficient H-donor, was used. The addition of increasing amounts of this compound in deaerated benzene solutions increased the ^3PN decay rate. Concomitantly, the appearance of a new species with the PN ketyl radical's spectrum could be clearly observed. From a Stern–Volmer plot (Fig. 4a), the rate constant for this reaction is calculated as $k_q = (4.9 \pm 0.4) 10^5 \text{ M}^{-1} \text{ s}^{-1}$. This value is in accordance with other rate constants known for the reaction of $\pi\pi^*$ triplet aromatic ketones with the same H-donor. For instance, the rate constant for acynaphthalene is 1×10^5 – $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [19].

The temperature dependence of this reaction was also investigated. In a 70 mM Bu_3SnH solution the lifetime of ^3PN decreases when the temperature increases, while in the absence of the H-donor it remains unaffected in the temperature range studied (Fig. 4b). The pseudofirst-order rate constant for H-abstraction from ^3PN ($k_H = k_q [\text{Bu}_3\text{SnH}]$) was calculated with the equation $k_H = k_T - k_T(0)$, where $k_T(0)$ and k_T are the rate constants for triplet decay in the absence and

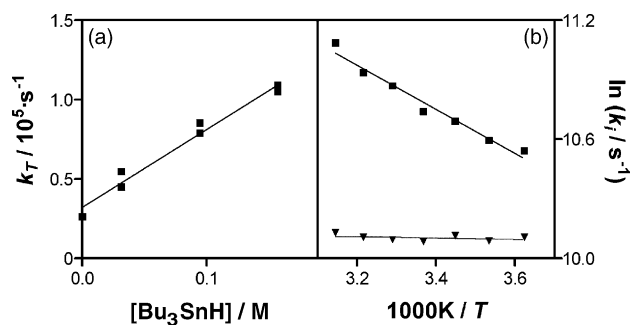


Fig. 4. (a) Stern–Volmer plot for ^3PN deactivation by Bu_3SnH in oxygen-free benzene at room temperature (k_T measured at 500 nm). (b) Arrhenius plot for $k_T(0)$ (▼) and k_H (■) (see Section 3 in the text).

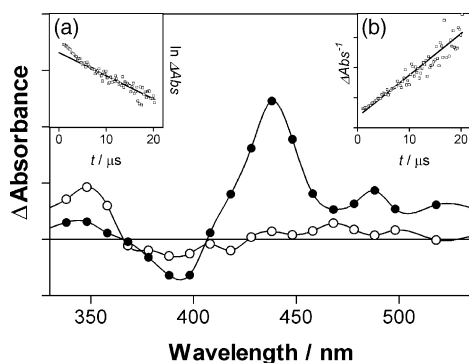


Fig. 5. Transient absorption spectra of PN (30 μM) in the presence of DABCO (1 mM) in argon-saturated acetonitrile after 1 μs (●) and 137 μs (○). Insets: (a) first- and (b) second-order kinetics fit to the decay at 440 nm over the first 20 μs .

in the presence of H-donor, respectively. From the slope of the Arrhenius plot for k_{H} , an activation energy $E_{\text{a}}^{\text{H}}(\pi\pi^*) = 9 \pm 1 \text{ kJ mol}^{-1}$ was calculated. For similar aromatic ketones with closely-lying $\pi\pi^*$ and $n\pi^*$ excited states, H-abstraction is usually assumed to proceed mostly from the thermally populated more reactive upper $n\pi^*$ state [19]. The activation energy can be thus related to the energy gap between the two triplets and the activation energy of the upper, more reactive, $n\pi^*$ state as $E_{\text{a}}^{\text{H}}(\pi\pi^*) = E_{\text{a}}^{\text{H}}(n\pi^*) + [E_{\text{T}}(n\pi^*) - E_{\text{T}}(\pi\pi^*)]$ [20]. Assuming in our case that the presence of the H-donor does not perturb the triplet energy levels, the measured activation energy, $E_{\text{a}}^{\text{H}}(\pi\pi^*)$, sets an upper limit value for the energy gap between the two triplets. The 9 kJ mol^{-1} value encountered is in agreement with that for other aromatic ketones, e.g. $10\text{--}13 \text{ kJ mol}^{-1}$ for *p*-anisyl alkyl ketones in nonpolar solvents [20,21]. Since T_1 ($\pi\pi^*$) of PN lies at 185 kJ mol^{-1} [2,22], the small energy difference between the two triplets confirms the hypothesis that T_2 ($n\pi^*$) in PN lies below S_1 (288 kJ mol^{-1}), thus explaining its fast intersystem crossing and high Φ_{T} [1]. Moreover, the energy gap between S_1 and T_2 is so large that it is unlikely that the two states reverse their energy, e.g., by increasing solvent polarity. Therefore, $\Phi_{\text{T}} \approx 1$ should be expected in all solvents, as experimentally observed [1].

To produce the PN radical anion, PN was irradiated in the presence of the electron donor DABCO in oxygen-free acetonitrile. Within 1 μs after the laser pulse, a transient species with a main absorption band at 440 nm was observed (Fig. 5). This band does not appear in the spectrum of ^3PN nor in that of the ketyl radical. The radical cation of DABCO is also ruled out since it absorbs weakly at around 460–480 nm [23–25]. Thus, we tentatively assign the band at 440 nm to the radical anion of PN. At longer timescales, a spectrum that resembles that of PN's ketyl radical appears, formed presumably by proton abstraction by the radical anion as reported for other aromatic ketones such as benzophenone [26,27]. The proton is thought to come from residual humidity of the solvent or from ground-state DABCO. In fact, meticulous drying of the solvent reduced the ampli-

tude of the longer-lived component, though it did not completely disappear. Second-order decay models fitted the data fairly well (Fig. 5, insets), consistent with radical ion recombination. Proton abstraction, although present, contributed only marginally to the decay kinetics as judged from the second-order plot.

In order to unveil the spectrum of the radical cation of DABCO, we performed the experiment in air-saturated solutions to selectively quench the PN radical anion by oxygen, a method already used by other authors [25,28]. In this case, the signal at 440 nm decayed with a first-order kinetics with time constant of ca. 300 ns, much faster than in oxygen-free solutions, which further supports its assignment to the radical anion of PN. Additionally, a slower component with a weak broad absorption band from 400 to 550 nm was present, which matches very well the reported radical cation of DABCO [24,25]. The lifetime of this long-lived transient was 120–140 μs .

Quenching of ^3PN by DABCO occurred with a rate constant approaching the diffusion control limit, i.e. $k_{\text{q}} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, typical of exergonic bimolecular electron transfer reactions [29]. This is consistent with our estimate of the driving force for this reaction, $\Delta_{\text{r}}G^0 = -30 \text{ kJ mol}^{-1}$, calculated using the Rehm–Weller Eq. (1) [29]:

$$\Delta_{\text{r}}G^0 = F[E(\text{D}^{\cdot+}/\text{D}) - E(\text{A}/\text{A}^{\cdot-})] - \Delta E_{00} - \frac{N_{\text{A}}e^2}{4\pi\epsilon_0\epsilon_{\text{r}}\epsilon_0} \quad (1)$$

where $E(\text{D}^{\cdot+}/\text{D})$ and $E(\text{A}/\text{A}^{\cdot-})$ are the oxidation and reduction potentials of donor and acceptor, respectively (0.57 [30] and -1.1 V versus SCE in this case), ΔE_{00} is the energy of the triplet state (185 kJ mol^{-1}) [2,22], and a is the donor–acceptor distance (typically 4 Å).

4. Conclusions

The kinetics of photochemical production and the difference absorption spectrum of the ketyl and anion radicals of PN have been characterized. H-abstraction by triplet PN occurs with an activation energy of 9 kJ mol^{-1} , consistent with a small energy gap between the $n\pi^*$ and the lower-lying $\pi\pi^*$ triplet states. This explains the high Φ_{T} in PN as well as its insensitivity to solvent polarity.

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References

- [1] E. Oliveros, P. Suardi-Muraseco, T. Aminian-Saghafi, A.M. Braun, H.-J. Hansen, *Helv. Chim. Acta* 74 (1991) 79–90.
- [2] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, *J. Photochem. Photobiol. A: Chem.* 79 (1994) 11–17.
- [3] C. Martí, O. Jürgens, O. Cuenca, M. Casals, S. Nonell, *J. Photochem. Photobiol. A: Chem.* 97 (1996) 11–18.
- [4] J.A. Leary, A.L. Lafleur, H.L. Liber, K. Blemann, *Anal. Chem.* 55 (1983) 758–761.
- [5] K. Winters, J.C. Batterton, C. Van Baalen, *Environ. Sci. Technol.* 11 (1977) 270–272.
- [6] R.G. Cooke, J.M. Edwards, *Prog. Chem. Org. Nat. Prod.* 40 (1981) 153–190.
- [7] J.G. Luis, W. Quiñones, F. Echeverri, T.A. Grillo, M.P. Kishi, F. Garcia-Garcia, F. Torres, G. Cardona, *Phytochemistry* 41 (1996) 753–757.
- [8] J.G. Luis, W.Q. Fletcher, F. Echeverri, T.A. Grillo, *Tetrahedron* 50 (1994) 10963–10970.
- [9] J.-Z. Xiao, S. Kumazawa, H. Tomita, N. Yoshikawa, C. Kimura, T. Mikawa, *J. Antibiot.* 46 (1993) 1570–1574.
- [10] A.V.B. Sankaram, M. Marthandamurthi, *Phytochemistry* 30 (1991) 359–360.
- [11] J.M. Kornfeld, J.M. Edwards, *Biochim. Biophys. Acta* 286 (1972) 88–90.
- [12] C. Stevenson, R.J. Davies, *Chem. Res. Toxicol.* 1999 (1999) 38–45.
- [13] A. Belvedere, F. Boscá, A. Catalfo, M.C. Cuquerella, G. De Guidi, M.A. Miranda, *Chem. Res. Toxicol.* 15 (2002) 1142–1149.
- [14] G.P. Rabold, K.H. Bar-Eli, E. Reid, K. Weiss, *J. Chem. Phys.* 42 (1965) 2438–2447.
- [15] H. Köller, G.P. Rabold, K. Weiss, T.K. Mukherjee, *Proc. Chem. Soc.* (1964) 332–333.
- [16] E. Oliveros, S.H. Bossmann, S. Nonell, C. Martí, G. Heit, G. Tröscher, A. Neuner, C. Martínez, A.M. Braun, *New J. Chem.* (1999) 85–93.
- [17] N.A. Kuznetsova, A.V. Reznichenko, V.N. Kokin, O.L. Kaliya, *J. Org. Chem. USSR (Engl. Transl.)* 18 (1982) 540–543.
- [18] T. Okutsu, S. Noda, S. Tanaka, A. Kawai, O. Kinichi, H. Hiratsuka, *J. Photochem. Photobiol. A: Chem.* 132 (2000) 37–41.
- [19] P. Wagner, B.-S. Park, in: A. Padwa (Ed.), *Organic Photochemistry*, vol. 11, Marcel Dekker Inc., New York, 1991, pp. 227–367.
- [20] M.V. Encina, E.A. Lissi, E. Lemp, A. Zanooco, J.C. Scaiano, *J. Am. Chem. Soc.* 105 (1983) 1856–1860.
- [21] P.J. Wagner, A.E. Kemppainen, H.N. Schoott, *J. Am. Chem. Soc.* 95 (1973) 5604–5614.
- [22] C. Flors, S. Nonell, *Helv. Chim. Acta* 84 (2001) 2533–2539.
- [23] G.T. Davis, M.M. Demek, D.H. Rosenblatt, *J. Am. Chem. Soc.* 94 (1972) 3321–3325.
- [24] D.A. Dunn, D.I. Schuster, *J. Am. Chem. Soc.* 107 (1985) 2802–2804.
- [25] C. Devadoss, R.W. Fessenden, *J. Phys. Chem.* 94 (1990) 4540–4549.
- [26] H. Miyasaka, K. Morita, K. Kamada, N. Mataga, *Chem. Phys. Lett.* 178 (1991) 504–510.
- [27] E. Haselbach, P. Jacques, D. Pilloud, P. Suppan, E. Vauthey, *J. Phys. Chem.* 95 (1991) 7115–7117.
- [28] J.C. Scaiano, L.C. Stewart, P. Livant, W. Majors, *Can. J. Chem.* 62 (1984) 1339–1343.
- [29] D. Rehm, A. Weller, *Isr. J. Chem.* 8 (1970) 259–271.
- [30] E. Vauthey, P. Suppan, E. Haselbach, *Helv. Chim. Acta* 71 (1988) 93–99.