

INTERACTION BETWEEN PHOTOGENERATED BIRADICALS AND FREE RADICALS: DI-TERT-BUTYLNITROXIDE

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Summary

Di-tert-butyl nitroxide interacts with the biradicals produced in the photochemistry of γ -methylvalerophenone with a rate k_s of $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene. This process leads to a change in the mode of biradical partition, which should be attributed to biradical-di-tert-butyl nitroxide interactions which reflect spin selection rules.

1. Introduction

Several reactions of photogenerated biradicals have been examined during the last few years [1 - 9]. In most cases these processes resemble those characteristic of the two radical sites involved; *e.g.* such is the case in hydrogen abstraction [1] and electron transfer reactions [3, 8]. There are only two well-documented systems in which the behaviour of biradicals is qualitatively and quantitatively different from that of monoradicals; the first is the interaction of molecular oxygen with biradicals generated in the Norrish type II process [4] and the second the interaction of di-tert-butyl nitroxide (DTN) with biradicals produced in some photocycloadditions [7]. Only the first system has been documented in both quantum yield and time resolved experiments. The common characteristic of these two systems is clearly the paramagnetic properties of the reagents involved, an aspect that deserves a closer examination. Free radicals can conceivably become useful probes to examine biradical behaviour, in particular lifetimes and multiplicity. With the exception of preliminary measurements from this laboratory [9] on the reactivity of biradicals from poly(phenyl vinyl ketone) towards DTN and nitric oxide, there are no reports in the literature on the absolute rates of interaction between free radicals and biradicals.

γ -Methylvalerophenone has proved to be an extremely convenient source of biradicals, since the precursor triplet state is very short lived ($\tau_T \approx 2 \text{ ns}$ in benzene) [10], and the biradicals produced in the triplet decay process with a quantum yield of unity [11] can be detected directly [12] and cleave to yield products that are easy to analyse (Fig. 1).

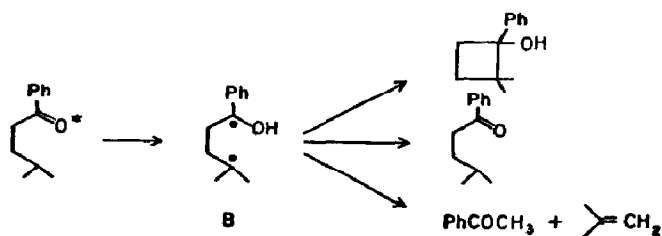


Fig. 1. Photochemistry of γ -methylvalerophenone.

We have examined the interaction of B with DTN using laser flash photolysis techniques as well as quantum yield studies. In combination, these methods provide information on the mechanism of reaction and the kinetics of the processes involved. A few exploratory experiments using galvinoxyl were also carried out.

2. Results

This section is divided according to the experimental technique used.

2.1. Laser flash photolysis

The samples were excited with pulses (337.1 nm, 8 ns, about 3 mJ) from a nitrogen laser. The transient absorptions due to the biradical B produced in reaction (1) were monitored directly at 415 nm [12] using a detection system with a nanosecond response. When DTN was added to the samples the rate of decay of B increased significantly (Fig. 2). Since in this system the decay of the triplet state can be formally regarded as an "instantaneous" process, the rate k_d of decay of B can be expressed by

$$k_d = \tau_B^{-1} + k_S[\text{DTN}] \quad (\text{I})$$

where τ_B is the biradical lifetime and k_S is the rate of biradical scavenging by DTN. We note that eqn. (I) does not involve any assumption about the nature of the molecular interactions involved in the scavenging process. The biradical decays observed followed clean first order kinetics and the corresponding plots of k_d versus [DTN] are illustrated in Fig. 2. The rate constants obtained in methanol and benzene are 2.5×10^9 and $1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ respectively. The intercepts are in good agreement with biradical lifetimes previously reported [3, 12].

2.2. Quantum yield studies

Examination of the quantum yield for acetophenone production shows that DTN causes an *increase* in this yield which is also accompanied by a parallel increase in the yield of 2-methylpropene. In earlier publications from this laboratory [4, 13] we have shown that the change in yields resulting from biradical processes can be correlated with rate parameters according to

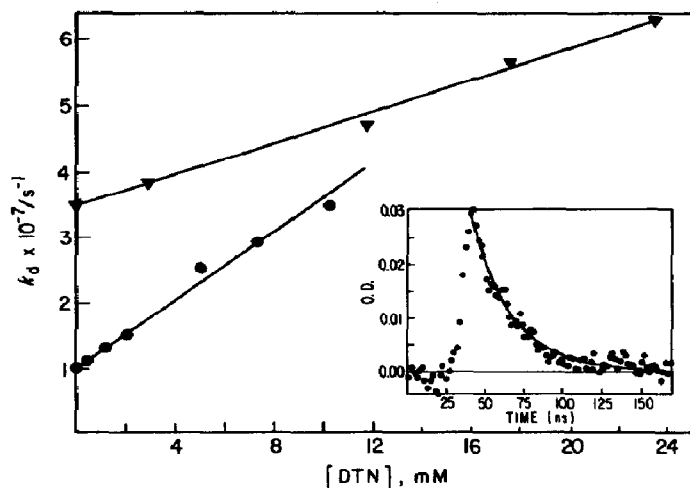


Fig. 2. Effect of DTN on the rates of biradical decay: \blacktriangledown , benzene; \bullet , methanol. Inset: typical trace in benzene for $[\text{DTN}] = 0.0029 \text{ M}$; the signal-to-noise ratio was considerably better in methanol.

$$\frac{\phi_{\text{II}}^0}{\phi_{\text{II}} - \phi_{\text{II}}^0} = \frac{1}{\epsilon} \left(1 + \frac{1}{k_{\text{S}} \tau_{\text{B}} [\text{DTN}]} \right) \quad (\text{II})$$

ϕ_{II}^0 and ϕ_{II} are the quantum yields of photofragmentation in the absence and presence of DTN and ϵ is the enhancement factor defined according to

$$\epsilon = \frac{\beta}{P_{\text{II}}} - 1 \quad (\text{III})$$

where P_{II} is the probability of fragmentation from B and β is the same probability for a biradical which interacts (associates?) with DTN. The enhancement factor is zero when the reagent considered does not affect the fraction of biradicals which give fragmentation products [4]. Figure 3 shows the effect of DTN on the yields according to eqn. (II). It should be noted that the enhancement of the yields cannot be attributed to a triplet state process because its short lifetime [10] would make its interaction with DTN inefficient. In fact, triplet quenching makes the enhancement of the yields somewhat smaller than could be expected from biradical scavenging alone. In order to correct for this effect we carried out some experiments with propiophenone, which cannot give biradicals but from the point of view of the triplet state can be regarded as a good model for γ -methylvalerophenone. From quenching experiments in which we monitored the decay of the triplet state at 390 nm (Fig. 4) we obtained $k_{\text{q}} = 2.25 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, a value that we assume is also applicable to γ -methylvalerophenone. Corrected quantum yields can be obtained using

$$\phi_{\text{II}}^{\text{c}} = \phi_{\text{II}} \frac{\tau_{\text{T}}^{-1} + k_{\text{q}} [\text{DTN}]}{\tau_{\text{T}}^{-1}} \quad (\text{IV})$$

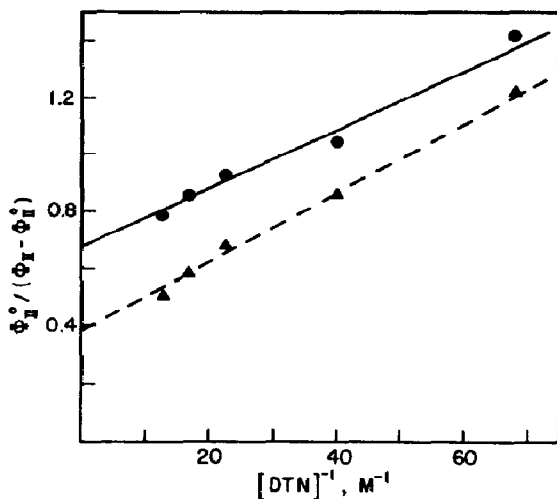


Fig. 3. Effect of DTN on the quantum yield of photofragmentation in benzene according to eqn. (II): ●, —, uncorrected data; ▲, ---, corrected data (see eqn. (IV)).

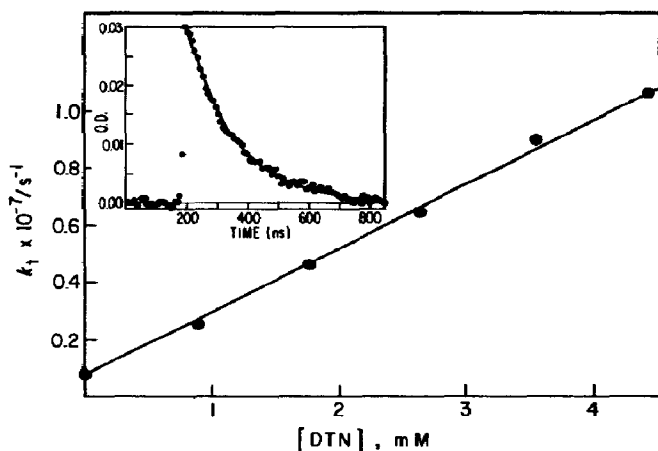


Fig. 4. Quenching of propiophenone triplets by DTN, monitored at 390 nm; k_1 is the rate constant for triplet decay. Inset: representative decay trace for $[DTN] = 0.00265 M$. The solvent was benzene.

where k_q is the rate constant for triplet quenching and ϕ_{II}^0 is the hypothetical quantum yield if triplet quenching could be totally avoided. Figure 3 also includes a corrected plot; from this plot and using eqns. (II) and (IV) we obtain $k_s\tau_B = 31 M^{-1}$ and $\epsilon = 2.72$. Taking into account that $P_{II} = 0.22$ [14] and using eqn. (III), we obtain $\beta \approx 0.82$, which, taking into consideration that a fraction of the biradicals yields cyclobutanols, means that essentially every biradical that interacts with DTN yields products.

We have also examined the effect of DTN on the cyclobutanol-to-fragmentation ratio in benzene (see eqn. (II)). The experiments were monitored by gas chromatography. We observed that the percentage of cyclobutanols changed from 11% [14, 15] in the absence of DTN to 12.5%

in the presence of 0.044 M DTN; *i.e.* the probability of biradical partition leading to cyclobutanols increases slightly more than the probability of fragmentation.

Finally, we also carried out a series of exploratory flash experiments using galvinoxyl which has a convenient spectral window in the 337 nm region and is a well-known free radical trap [16]. We could not detect any bleaching under conditions where predictions based on biradical lifetimes and radical-like rates of reactions would have predicted a detectable change.

3. Discussion

The first point that should be noted is that the effect of DTN on the quantum yields cannot be attributed to a hydrogen bonding type of mechanism of the type proposed for alcohols, pyridine [17] and organophosphorus compounds [13]. Even highly effective reagents like pyridine and trimethylphosphate do not approach DTN in the magnitude of the effect or the rate of interactions.

The discussion which follows is based on the idea that the effect of DTN on the partition of the biradical is directly related to its paramagnetic properties; as shown in the previous section, triplet quenching effects, which have also been documented in the literature [18] can be easily corrected for. Further, it should be clear that the enhancement of the yields is a directly measurable effect, which is easily detected *before* any corrections are introduced.

Earlier reports from this laboratory have shown that the lifetime of B is controlled by its rate of intersystem crossing [3, 4]; therefore, the process discussed in this paper involves the interaction between a triplet and a doublet, for which spin selection rules predict that two-thirds of the encounters would be of a dissociative (quartet states) nature. In other words the rate of interaction cannot exceed one-third of diffusion control, in agreement with the experimental rate constants.

In the case of oxygen effects [4] we have observed values of β which were systematically around 0.75 while a hydroperoxide was formed with a 25% probability; this partition reflected the probability of triplet and singlet encounters respectively. The β value in the DTN system is close to unity, indicating that "doublet" encounters lead to characteristic type II products. Interestingly, in a related system, the photolysis of cycloalkanones in the presence of nitric oxide [5], one of the reaction products was a cyclic nitroxide radical, indicating that when alternative doublet reaction paths become available the process can lead to new products.

It is important to remember that all the modes of biradical decay illustrated in Fig. 1 require intersystem crossing; in other words all reaction paths lead to ground state products [11]. As a result, mere assisted intersystem crossing cannot explain the change in the way in which B partitions into products. Further, while DTN seems to favour fragmentation in the case

of γ -methylvalerophenone, it has been shown to prevent this mode of reaction in other systems [7]; therefore, the nature of the reaction path favoured is not a characteristic of DTN by itself. Two types of mechanism can be proposed: (1) the formation of a "true" intermediate, involving some kind of bonding (not necessarily covalent) which then leads to partition in a mode characteristic of this intermediate rather than that of the free biradical; (2) a spin-spin interaction *not* involving any direct association between the two species, in which case assisted intersystem crossing would have to be favoured for some conformations that differ from those in the free biradical. There is no conclusive evidence for one or the other mechanism in this paper or in the literature and, while the formation of a hydroperoxide in the presence of oxygen [4] and the generation of cyclic nitroxides in the case of nitric oxide [5] would indicate that a "true" intermediate can be formed, its formation could follow the initial interaction rather than be the driving force of the overall process.

While the detailed nature of the interactions involved may be still unclear, the possibility of changing the reaction path of photochemical processes, combined with the high efficiency with which these interactions take place can be of interest not only to the physical chemist, but also to the organic photochemist interested in increasing the yields and in speeding up specific photoprocesses. In addition, DTN may prove to be a useful reagent in studying biradical processes, in particular in determining their lifetimes and multiplicities. We hope that our direct measurements of the rate constants for this interaction will be useful for this purpose.

4. Experimental

4.1. Materials

DTN was an Eastman product and was used as received. Other chemicals were obtained from the same sources and were purified by the same methods as in earlier reports [3, 4, 13].

4.2. Quantum yield studies

Deaerated samples were contained in matched tubes made of precision bore tubing (i.d. 0.2500 ± 0.0002 in, made of Corning 7740 glass, Lab Crest Scientific). They were simultaneously irradiated in a merry-go-round apparatus using a Rayonet reactor fitted with 16 RPR-3500 lamps. Conversions, based on parent ketone, were kept below 2%.

4.3. Laser flash photolysis

The samples were excited using the pulses from a Moletron UV-400 nitrogen laser. The signals from an RCA-4840 photomultiplier tube were terminated into 93Ω and into a Tektronix R7912 transient digitizer. These signals were then averaged and processed using a PDP 11/55 computer. Further details have been given elsewhere [3, 8].

Acknowledgments

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