Preliminary Note

Excited state quenching by di-t-butyl nitroxide

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Di-t-butyl nitroxide (DTBN) is known to be an excellent quencher of the triplet states of ketones [1] and aromatic hydrocarbons [1, 2], and it has been used extensively in mechanistic photochemistry, although complications from radical trapping reactions are possible [3]. It is also known that the singlet states of aromatic hydrocarbons are quenched by DTBN [4, 5]. Singlet quenching was initially the subject of controversy as an early report indicated a decrease in the quenching rate constant with decreasing singlet energy of the quenchee [4]. However, a more recent study concluded that this was in error and the quenching rate is independent of singlet energy [5].

In spite of the extensive use of DTBN as a triplet quencher in mechanistic studies involving ketone photochemistry [6 - 10] there are significant gaps in our knowledge of its quenching abilities particularly with respect to the quenching of carbonyl singlet states. To learn more about DTBN as a quencher, especially regarding its use as a mechanistic probe of the photochemistry of ketones, we have studied room temperature fluorescence quenching using donors of varying types and singlet energies (Table 1). We have, in addition, briefly examined the quenching of phosphorescence in room temperature fluid solutions (Table 2) to compare the singlet *vs.* triplet quenching abilities of DTBN under comparable conditions.

Several conclusions can be drawn from our results. We confirm the lack of dependence of singlet quenching rate on singlet energy and find that the quenching rate constants approach diffusion control for all compounds independent of chromophore and solvent. Because the numerical values of the singlet quenching rate constants depend on the value chosen for singlet lifetime, we have, in several cases, directly compared the fluorescence quenching abilities of DTBN and *trans*-1, 3-pentadiene as this ratio is independent of singlet lifetime and conjugated dienes have previously been used to quench the singlet states of both carbonyl compounds [11] and aromatic hydrocarbons [12]. The extremely rapid singlet quenching rate constants have implications in the use of DTBN in mechanistic photochemical studies. Thus, the possibility of singlet quenching must not be ignored in making

TABLE 1

Fluorescence quenching by DTBN[a]

	Solvent	Concentration	E^{S} [b] (kcal/mol)	$k_q^S \tau^S$ [c] (M^{-1})	τ^S [d] (ns)	$k_q^S \times 10^{-10}$ [e] ($M^{-1}s^{-1}$)	$\dfrac{k_q^S(DTBN)}{k_q^s(diene)}$
acetone	cyclohexane	0.49 M	90	21	2.0^f	1.0	220
camphor	cyclohexane	0.02 M	90	31	4.1^g	0.7	170
9-methyl-anthracene	cyclohexane	$2.2 \times 10^{-4}M$	73	57	4.6^h	1.2	500
	acetonitrile	$2.2 \times 10^{-4}M$		137	4.6	3.0	—
biacetyl	benzene	0.05 M	65	167	14^i	1.2	—
benzil	benzene	0.029 M	65	34	2.0^j	1.7	—
	cyclohexane	0.012 M		40	2.0	2.0	570
eosin Y	acetronitrile	3.6×10^{-5}g/ml	54	39	4.5^h	0.9	—
rubrene	cyclohexane	$5.3 \times 10^{-5}M$	54	45	14.9^h	0.3^k	210
fluorescein	0.1 N NaOH	3.2×10^{-5}g/ml	53	35	4.0^h	0.9	—
rhodamine B	water	1.2×10^{-5}g/ml	53	11	3.2^h	0.3^l	—

[a] Room temperature aerated solutions. [b] Approximate (0,0) absorption. [c] Slope of Stern–Volmer quenching plot, estimated error = 10%. [d] Singlet lifetimes, literature values. [e] Bimolecular rate constant for quenching. [f] F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro and J. C. Dalton, J. Am. Chem. Soc., 92 (1970), 1793. [g] N. J. Turro et al., J. Am. Chem. Soc., 92 (1970), 6978. [h] Taken from I. B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1971, 2nd Edn. [i] N. J. Turro and R. Engel, J. Am. Chem. Soc., 91 (1969), 7113. [j] A. Yekta, Ph. D. Dissertation, Columbia University, (1973). [k] From ref. [7], $k_q^S = 2.1 \times 10^9$ in methylcyclohexane. [l] From ref. [7], $k_q^S = 4.7 \times 10^9$ in methylcyclohexane.

TABLE 2

Phosphorescence quenching by DTBN[a]

	Solvent	E^{T} [b] (kcal/mol)	$k_q^T \tau^T \times 10^{-5}$ [c] (M^{-1})	$\tau^T \times 10^3$ [d] (s)	$k_q^T \times 10^{-9}$ [e] ($M^{-1}s^{-1}$)
benzophenone	perfluoromethyl-cyclohexane (0.0012 M)	69	5.3	0.71^f	0.8^g
benzil	benzene (0.01 M)	53	2	0.32^h	0.6
	cyclohexane (0.01 M)	53	1.4	0.32	0.4

[a] Degassed solutions. [b] Approximate (0,0) of phosphorescence. [c] Slope of Stern–Volmer quenching plot, estimated error ± 25%. [d] Phosphorescence lifetimes, literature values. [e] Bimolecular rate constant for quenching. [f] C. A. Parker and T. Joyce, J.C.S., Chem. Commun., (1968), 749. [g] Ref. [8] reports $k_q^T = 2.6 \times 10^9$ in benzene. [h] M. Almgren. Photochem. Photobiol., 6 (1967), 879.

mechanistic conclusions since the rather large Stern–Volmer slopes observed for singlet quenching might easily and erroneously be interpreted in terms of a triplet quenching mechanism.

DTBN quenching of the room temperature phosphorescence from carbonyl compounds (biacetyl, benzil and benzophenone) was complicated by changes in the observed phosphorescence intensities during spectroscopic examination of the degassed samples. These changes were only observed in samples containing DTBN; and in samples containing very low DTBN concentrations ($\sim 10^{-6}M$) the final phosphorescence intensities were actually greater than samples without DTBN. This behavior was independent of solvent (methylcyclohexane, cyclohexane, acetonitrile or benzene) and the method of purification, The observations suggested that DTBN was being destroyed in the spectrophotometer perhaps with concomitant loss of quenching impurity present initially in very low concentration. This was confirmed my monitoring the e.s.r. signal of DTBN (10^{-5} M) during irradiation [13]. The signal was unchanged in the dark but an 8% decrease was noted on irradiation for one hour. A similar DTBN solution containing 0.01 M biacetyl or benzophenone showed a decrease of 77% over the same irradiation time period. We do not wish to speculate on the mechanistic nature of our observations at this time [14] but we do want to emphasize the complications this would introduce into a mechanistic study. We have minimized this complication in our phosphorescence quenching experiments by carefully shielding our samples from light during preparation and using only initial phosphorescence intentities in our Stern–Volmer plots. Because of these difficulties, biacetyl phosphorescence quenching could not be determined but satisfactory data were obtained for benzophenone and biacetyl. Comparison of the rates of DTBN quenching of benzil singlets and triplet states indicates that the rate of singlet quenching may be greater than that for the triplet. This result underscores our caution in the use of DTBN as a photochemical mechanistic probe.

In conclusion, DTBN is an effective quencher of both singlet and triplet states; therefore, care must be exercised in the interpretation of results obtained from its use as a mechanistic probe. In addition, one must be cognizant of the possibility of a donor required photodestruction of small amounts of DTBN in a photochemical or even a spectroscopic experiment.

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14 We believe it likely that traces of oxygen, remaining in even carefully degassed solutions, are involved in the observed DTBN depletion.