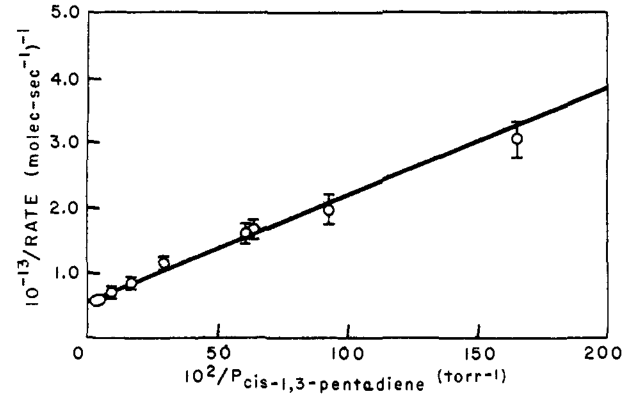

Figure 12. Reciprocal isomerization rate *vs.* reciprocal pressure of *cis*-1,3-pentadiene.

In this hypothesis, step 4 must embody the following processes.

$$(\text{SD})^* \longrightarrow {}^3(\text{SD}) \qquad (4a)$$

$$^3(\text{SD}) \longrightarrow (\text{SD}) \qquad (4b)$$

$$cis\text{-D} + {}^3(\text{SD}) \longrightarrow {}^3\text{D} + \text{SD} \qquad (4c)$$

The rate law derived on this basis (assuming $\theta = 1$) is

$$\text{rate}_{c\rightarrow t} = \frac{k_7 k_{4a} k_{4c} k_2 I_0[cis\text{-D}]}{(k_{4b} + k_{4c}[cis\text{-D}])(k_3 + k_{4a} + k_5)(k_6 + k_7)}$$

The form of the rate law is unchanged if (4c) involves physically adsorbed diene. It should be noted that two types of adsorption are suggested here. In the first type light absorbing species are formed between "active" sites on the Pyrex surface and 1,3-pentadiene. This type of adsorption is complete at very low pressure. This second type of adsorption possibly important in eq 4c is physical and readily reversible. A plot of 1/rate *vs.* 1/*P* using data presented in Figure 10 for pressures ranging from the highest down to 0.54 Torr appears to be linear as required by this mechanism (Figure 12).

To account for the effect of added gases oxygen and 1,3-butadiene, eq 4d is included.

$$^3(\text{SD}) + \text{M} \longrightarrow \text{OUT} \qquad (4d)$$

For constant [*cis*-D], a plot of (rate without added gas)/(rate with added gas) *vs.* pressure of added gas should give a straight line with an intercept of unity. This is the case within the error limits of the data in Figure 11. A competitive adsorption mechanism probably could explain the data as well.

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Quenching of Excited States by Stable Free Radicals. II.[1] On the Mechanism of Triplet Quenching by Di-*tert*-butyl Nitroxide

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Abstract: The overall rate constants (k_q) for the quenching of a number of aromatic hydrocarbon and ketone triplets by di-*tert*-butyl nitroxide (DTBN) in fluid solution have been measured. The values of k_q decrease in the order stilbene ≈ diffusion controlled > ketones > hydrocarbons, and show no correlation with triplet energies. The data are consistent with vibrational relaxation of the triplet *via* intersystem crossing to the ground-state vibrational manifold, which is made spin allowed by electron spin exchange with DTBN. This behavior of DTBN is contrasted with triplet quenching by other paramagnetic species, and several potential applications to photochemistry are discussed.

The deactivation of electronically excited molecules by paramagnetic species is a phenomenon which has received widespread interest from spectroscopists and photochemists for some time. It may reasonably be expected that transitions which are normally spin forbidden will become at least partially spin allowed in the presence of a paramagnetic quencher, providing pathways for deactivation are not available to diamagnetic quenchers or to the excited molecule itself. Clear-cut experimental evidence regarding the nature of paramagnetic quenching has been difficult to obtain, however, because of the variety of competing processes and experimental complications encountered in many studies. For instance, molecular oxygen, that most ubiquitous of paramagnetic molecules, is an exceedingly efficient quencher of photoexcited singlets and triplets.[3,4] This

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(1) Part I: R. A. Caldwell and Robert E. Schwerzel, *J. Amer. Chem. Soc.*, **94**, 1035 (1972).

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has been attributed both to enhanced singlet–triplet transitions resulting from interactions with the triplet spin of ground-state oxygen and to the presence of low-lying singlet excited states of oxygen;[5] indeed, the dominant pathway for triplet quenching by oxygen embodies both of these features.[5b,c]

$$^3M + {}^3O_2 \longrightarrow M + {}^1O_2 \qquad (1)$$

Similarly, nitric oxide, a doublet ground-state molecule, is known to quench singlets and triplets nearly as efficiently as oxygen.[6,7] Since energy transfer to nitric oxide is improbable for most organic singlets and triplets in condensed media,[7,8] it is likely that the rapid quenching results from spin-conserved relaxation of the excited state as first suggested by Porter and Wright;[7] this is illustrated for triplet quenching by reaction 2.

$$^3M + {}^2NO \longrightarrow M + {}^2NO \qquad (2)$$

It should be pointed out that the high reactivity of both oxygen and nitric oxide is potentially a problem, since chemical reaction with an excited molecule could give "quenching" which could be misinterpreted as occurring by reactions 1 or 2.

A number of workers have investigated triplet quenching by paramagnetic metal ions and complexes.[7,9–12] While there is some evidence for the operation of a process analogous to reaction 2 in a few cases,[7,10] these studies are greatly complicated by solvation of the ions and by energy transfer and/or photoreactions involving the metal complexes.[11,12]

The theory of paramagnetic quenching has evolved along the idea of "catalyzed spin conservation" (reaction 2) developed by Porter and Wright.[7] Murrell[13] has treated the effect of paramagnetic molecules on radiative transitions both in terms of spin-enhanced singlet–triplet mixing in the excited species and in terms of charge-transfer complex formation in the excited state (particularly as applied to oxygen quenching).[5a] Hoytink,[14] noting that according to Porter and Wright the total spin of the triplet-quencher system is conserved during the quenching process,[15] has pointed out that this implies that electron spin exchange between the two interacting species is primarily responsible for the enhanced rate of singlet–triplet transitions. This in turn leads to the interesting prediction[14] that (1) the electronic excitation energy will remain on the triplet molecule throughout the interaction with the quencher, and (2) radiationless quenching will proceed by vibrational relaxation of the triplet *via* intersystem crossing to the ground-state vibrational manifold, which is made spin allowed by the exchange process. We will return to these points later on.

A number of authors have recently turned their attention to the question of quenching by stable free radicals (as opposed to the use of stable radicals as scavengers of transient free radicals[16]). Ern and Merrifield[17a] have shown that anthracene triplet excitons are quenched by radicals produced when crystalline anthracene is subjected to X-irradiation, while Yang and Murov[17b] have implicated transient ketyl radicals as quenchers in the solution photoreduction of benzophenone.

Other workers have reported the use of stable free radicals as quenchers of reactive intermediates in photochemical reactions.[1,18,19] These studies have generally involved the use of di-*tert*-butyl nitroxide (DTBN);[20] this radical is quite stable, is easily purified, and has a convenient absorption window around 360–380 nm. One exception is the work of Faulkner and and Bard,[19] who found that Wurster's Blue perchlorate is an effective (but not entirely diffusion-controlled) quencher of anthracene triplets.

It seems to have been generally *assumed* that DTBN quenches triplets at a diffusion-controlled rate,[18d] although this is supported by little concrete evidence. Indeed, Chapman has reported that the addition of 4,4-dimethylcyclohexanone to ketene acetal leading to cis adduct is quenched by DTBN more rapidly than the reaction leading to trans adduct;[18c] this has been interpreted in terms of differential quenching of two triplet exciplexes.[18e] It is of interest also that Singer has found that DTBN is capable of quenching both the singlet and triplet excited states of fluorenone.[18d]

Our curiosity about the interactions between free radicals and excited species, and the current lack of coherent experimental evidence, promoted us to undertake a systematic study of triplet quenching by DTBN in solution. We have previously reported some preliminary results of this study,[1] which indicated that DTBN quenching of benzophenone and stilbene triplets is much more rapid than the quenching of naphthalene triplets. We present here more complete results and a discussion of the mechanistic implications of this work.

Results and Discussion

Kinetic Analysis. The overall rate constants for

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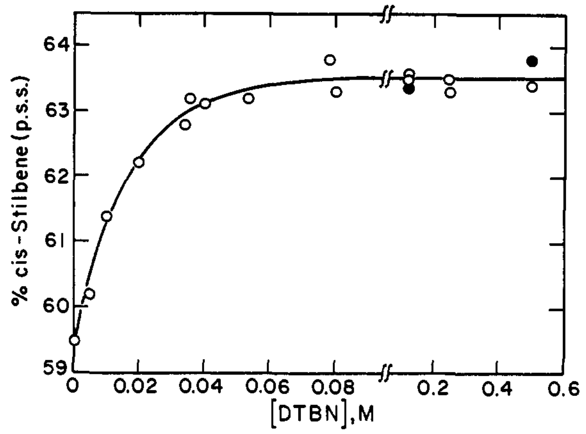

Figure 1. Variation of benzophenone-sensitized stilbene photostationary state composition with different nitroxide concentration. Irradiation at 366 nm, in degassed benzene solution, [benzophenone] = 0.050 *M*, [*trans*- (or *cis*-) stilbene] = 0.025 *M*: (○) starting with *trans*-stilbene, (●) starting with *cis*-stilbene.

DTBN quenching of a number of triplet sensitizers have been measured in degassed fluid solution at 27°. In general, those sensitizers which absorb strongly at 366 nm and intersystem cross with unit efficiency to their triplet manifold were irradiated directly. To avoid complications arising from singlet sensitization and/or competitive absorption by the DTBN, benzophenone was used as a triplet sensitizer for all of the other sensitizers which were studied.[21] The quenching process was then monitored by observing the extent of triplet-sensitized trans–cis isomerization of stilbene; this system has been studied extensively and seems to be well understood.[22] Details of the procedure may be found in the Experimental Section.

Providing that sufficient added sensitizer is present to cause detectable (or predominant) stilbene isomerization *via* energy transfer from the sensitizer triplet, the system is adequately described by the following kinetic scheme, in which B = benzophenone; H = added sensitizer, usually an aromatic hydrocarbon; TS, CS = *trans*- and *cis*-stilbene, respectively; ^{3}S = twisted stilbene triplet; and N = DTBN. We assume that the quantum yield for production of benzophenone triplets is unity,[23] and that quenching of benzophenone triplets by other species is rapid compared with thermal repopulation of the excited singlet state.[24]

Excitation

$$\mathrm{B} \xrightarrow{h\nu} {}^1\mathrm{B} \longrightarrow {}^3\mathrm{B} \tag{3}$$

Benzophenone quenching

$$^3\mathrm{B} + \mathrm{H} \xrightarrow{k_\mathrm{H}} {}^3\mathrm{H} + \mathrm{B} \tag{4}$$

$$^3\mathrm{B} + \mathrm{TS} \xrightarrow{k_\mathrm{TS}} {}^3\mathrm{S} + \mathrm{B} \tag{5}$$

$$^3\mathrm{B} + \mathrm{N} \xrightarrow{k_\mathrm{N}} \mathrm{B} + \mathrm{N} \tag{6}$$

Sensitizer quenching

$$^3\mathrm{H} + \mathrm{TS} \xrightarrow{k_\mathrm{HTS}} {}^3\mathrm{S} + \mathrm{H} \tag{7}$$

$$^3\mathrm{H} + \mathrm{N} \xrightarrow{k_\mathrm{q}} \mathrm{H} + \mathrm{N} \tag{8}$$

Stilbene triplet decay

$$^3\mathrm{S} \xrightarrow{k_\mathrm{C}} \mathrm{CS} \tag{9}$$

$$^3\mathrm{S} \xrightarrow{k_\mathrm{T}} \mathrm{TS} \tag{10}$$

$$^3\mathrm{S} + \mathrm{N} \xrightarrow{k_\mathrm{NC}} \mathrm{CS} + \mathrm{N} \tag{11}$$

$$^3\mathrm{S} + \mathrm{N} \xrightarrow{k_\mathrm{NT}} \mathrm{TS} + \mathrm{N} \tag{12}$$

Reactions 11 and 12 are included because we have previously shown[1] that DTBN quenches stilbene triplets at approximately the diffusion-controlled rate, and that in doing so perturbs the normal decay mode of ^{3}S. This behavior is illustrated in Figure 1, which shows the effect of varying concentrations of DTBN on the photostationary state composition of degassed benzene solutions containing 0.025 *M trans*- or *cis*-stilbene and 0.050 *M* benzophenone. We define the decay ratio of ^{3}S in the absence of DTBN as

$$\alpha_\mathrm{O} = k_\mathrm{C}/(k_\mathrm{C} + k_\mathrm{T}) \tag{13}$$

and in the presence of concentrations of DTBN sufficient to perturb the photostationary state composition as

$$\alpha_\mathrm{N} = \frac{k_\mathrm{C} + k_\mathrm{NC}[\mathrm{N}]}{k_\mathrm{C} + k_\mathrm{T} + (k_\mathrm{NC} + k_\mathrm{NT})[\mathrm{N}]} \tag{14}$$

In the limiting region above [DTBN] = *ca.* 0.1 *M*, it may be assumed that $k_\mathrm{NC}[\mathrm{N}] \gg k_\mathrm{C}$ and that $(k_\mathrm{NC} + k_\mathrm{NT})[\mathrm{N}] \gg (k_\mathrm{C} + k_\mathrm{T})$ so that

$$\alpha_\mathrm{N}(\mathrm{lim}) = k_\mathrm{NC}/(k_\mathrm{NC} + k_\mathrm{NT}) \tag{15}$$

Equations 13–15 thus provide a description of the behavior illustrated in Figure 1. In our quenching-rate studies, concentrations of DTBN from 0 to 0.020 *M* were employed, and the appropriate values of α_N were determined directly from Figure 1 at each nitroxide concentration.[1,22a]

Since the observed quantum yield for stilbene isomerization, Φ_TC, contains contributions from reactions 5 and 7, it may be expressed as

$$\Phi_\mathrm{TC} = \Phi_\mathrm{BTC} + \Phi_\mathrm{BH} f_\mathrm{HTC} \tag{16}$$

where Φ_BTC = quantum yield of benzophenone-sensitized isomerization, Φ_BH = quantum yield of benzophenone-sensitized sensitizer triplet formation, and f_HTC = fraction of sensitizer triplets which produce isomerization. Solving the steady-state expressions for excited species, we obtain

$$\Phi_\mathrm{BTC} = \frac{\alpha_\mathrm{N} k_\mathrm{TS}[\mathrm{TS}]}{k_\mathrm{H}[\mathrm{H}] + k_\mathrm{TS}[\mathrm{TS}] + k_\mathrm{N}[\mathrm{N}]} \tag{17}$$

$$\Phi_\mathrm{BH} = \frac{k_\mathrm{H}[\mathrm{H}]}{k_\mathrm{H}[\mathrm{H}] + k_\mathrm{TS}[\mathrm{TS}] + k_\mathrm{N}[\mathrm{N}]} \tag{18}$$

$$f_\mathrm{HTC} = \frac{\alpha_\mathrm{N} k_\mathrm{HTS}[\mathrm{TS}]}{k_\mathrm{HTS}[\mathrm{TS}] + k_\mathrm{q}[\mathrm{N}]} \tag{19}$$

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[21] The molar extinction coefficient of benzophenone is *ca.* 100 times that of DTBN at the wavelength of the exciting light (366 nm). Since the absorbance of 0.050 *M* benzophenone is *ca.* 4 at 366 nm, we conclude that neither DTBN nor the added sensitizers used in this study absorb light.

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Since the triplet excitation transfer processes of reactions 4, 5, and 7 are all exothermic by at least 4–5 kcal/mol, we assume that they all proceed at a diffusion-controlled rate;[25] that is, $k_H = k_{TS} = k_{HTS} = k_{diff}$. Further, since we have shown[1] that $k_N = 2.6 \times 10^9\ M^{-1}\ sec^{-1}$, we may set $k_N = k_{diff}/2$, assuming a diffusion-controlled rate constant of $5.0 \times 10^9\ M^{-1}\ sec^{-1}$ in benzene.[25] Making the appropriate substitutions and rearranging eq 16, we obtain

$$f_{HTC} = \frac{\Phi_{TC} - \{\alpha_N[TS]/([H] + [TS] + [N]/2)\}}{[H]/([H] + [TS] + [N]/2)} \qquad (20)$$

This equation allows us to extract the value of f_{HTC} from the observed quantum yield, Φ_{TC}, simply by applying correction terms based on the known concentrations of reagents and on the known values of α_N. The calculated values of f_{HTC} may then be treated by the Stern–Volmer approach. In the absence of added DTBN, we may write

$$f^{O}_{HTC} = \alpha_O k_{HTS}[TS]/k_{HTS}[TS] = \alpha_O \qquad (21)$$

while in the presence of DTBN the value of f^{N}_{HTC} is given by eq 19. Thus, one obtains eq 22, which predicts that plots of $(\alpha_N/\alpha_O)(f^{O}_{HTC}/f^{N}_{HTC})$ against [N] should be linear with slope $= k_q/k_{HTS}[TS] = k_q/k_{diff}[TS]$.

$$\frac{f^{O}_{HTC}}{f^{N}_{HTC}} = \left(\frac{\alpha_O}{\alpha_N}\right)\left(1 + \frac{k_q[N]}{k_{HTS}[TS]}\right) \qquad (22)$$

This behavior is illustrated in Figure 2, which shows Stern–Volmer plots for the quenching of benzophenone-sensitized naphthalene and naphthalene-d_8 by DTBN. Since the concentration of naphthalene is much greater than that of stilbene or of DTBN, most of the benzophenone triplets transfer energy to naphthalene; the competing processes thus make relatively small contributions to the quenching of benzophenone, as assumed above. Similar linear plots were obtained for all sensitizers for which competitive absorption by sensitizer and/or singlet sensitization were not significant.[21] These complications were encountered with triphenylene, chrysene, and 2,2′-dinaphthyl (for which competitive light absorption was anticipated) as evidenced by the complete lack of any correlation of the data from these runs with eq 22. Such sensitizers were therefore omitted from this study. In the case of biphenyl a linear plot was obtained, but the assumption that $k_{HTS} = k_{diff}$ breaks down since Wagner[26] has shown that energy transfer from benzophenone to biphenyl is slow and reversible. The reported[26] value of k_H for benzophenone–biphenyl in benzene (corrected for reversibility) is ca. $2.5 \times 10^8\ M^{-1}\ sec^{-1}$, so as a reasonable approximation one may write $k_H \approx k_{diff}/20$. Equation 20 thus becomes, in this case

$$f_{HTC} = \frac{\Phi_{TC} - \left(\dfrac{\alpha_N[TS]}{[H]/20 + [TS] + [N]/2}\right)}{\left(\dfrac{[H]/20}{[H]/20 + [TS] + [N]/2}\right)} \qquad (23)$$

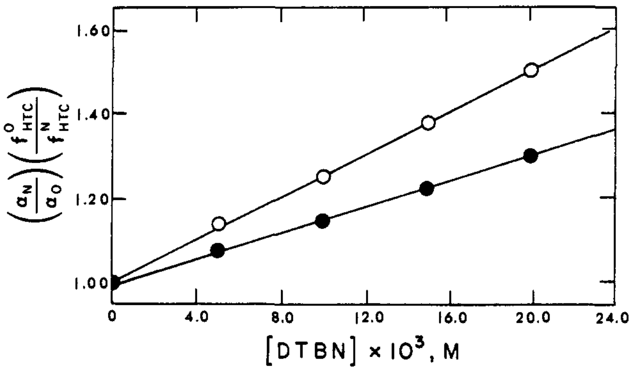

Figure 2. Stern–Volmer plot of the quenching of benzophenone-sensitized hydrocarbon triplets by DTBN; irradiation at 366 nm, in degassed benzene solutions, [benzophenone] = 0.050 *M*, [*trans*-stilbene] = 0.005 *M;* [hydrocarbon] = 0.100 *M:* (○) naphthalene, slope = 25.0 M^{-1}; (●) naphthalene-d_8, slope = 15.2 M^{-1}.

Finally, there may be a small systematic error in the absolute values of k_q for the quenching of benzophenone and fluorenone in cyclohexane,[27] since in this solvent k_{diff} is calculated to be about 70% as large as k_{diff} in benzene.[28] We consider this error to be small compared with the potential (but unknown) errors inherent in the assumption that $k_{diff} = 5.0 \times 10^9\ M^{-1}\ sec^{-1}$ in benzene for all the systems studied here, and therefore this value of k_{diff} has been used in calculating the values of k_q in cyclohexane as well. The salient point is that, whatever the "true" value of k_{diff} in cyclohexane, fluorenone is quenched at essentially the same rate as benzophenone in this solvent.

Quenching Rate Constants. The measured values of k_q are presented in Table I along with the triplet energies of the sensitizers studied. It is immediately obvious that the rate constants show no correlation with E_T and that the general trend in the values of k_q is stilbene

Table I. Rates of Triplet Quenching by DTBN[a]

Triplet	k_q, M^{-1} sec^{-1} [b]	E_T, kcal/mol[c]
Stilbene	ca. 50 × 10^8 [d]	ca. 48[e]
Biacetyl	37 × 10^8	55
Benzophenone	26 × 10^8	69
Benzophenone[f]	13 × 10^8	69
Fluorenone[g]	15 × 10^8	53
Biphenyl	7.0 × 10^8	69
Phenanthrene	6.4 × 10^8 [h]	62
Naphthalene	6.3 × 10^8	61
3-Acetylphenanthrene	6.0 × 10^8 [i]	59
1-Bromonaphthalene	5.2 × 10^8 [h]	59
Naphthalene-d_8	3.7 × 10^8	60

[a] Measured in degassed benzene solutions containing 0.005 *M* *trans*-stilbene, 0.050 *M* benzophenone, and 0.100 *M* sensitizer, unless indicated otherwise; irradiation at 366 nm. [b] Estimated precision $\overline{<} \pm 5.0\%$, based on reproducibility of duplicate runs. [c] Taken from ref 23b. [d] Estimated from photostationary state data; see ref 1. [e] See ref 22a and 22d. [f] Cyclohexane solution,[27] same concentrations as in benzene. [g] Cyclohexane solution[27] containing 0.005 *M* *trans*-stilbene and 0.010 *M* fluorenone. [g] Estimated precision, ca. ±10%. [i] Direct irradiation in benzene solution containing 0.005 *M* *trans*-stilbene and 0.050 *M* 3-acetylphenanthrene.

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(26) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967).

(27) Cyclohexane was used in comparing the rates of DTBN quenching of benzophenone and fluorenone since both ketones intersystem cross to their excited triplet states with unit efficiency in this solvent;[22f] in benzene, ϕ_{isc} for fluorenone = 0.93.[22f]

(28) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

> n–π^* ketone triplets > π–π^* hydrocarbon triplets. This trend, and the lack of correlation with E_T, argues strongly against any quenching process involving transfer of excitation energy to DTBN; were this the case, k_q would be expected[25] to remain essentially constant at or near k_{diff} until the sensitizer E_T became roughly equal to the excitation energy of DTBN. This, in turn, suggests that the behavior of DTBN is analogous to that of nitric oxide.[6–8]

Closer examination of Table I reveals that the data are fully consistent with exchange-induced quenching, as developed by Hoytink.[14] In this view, the triplet and DTBN are presumed to interact sufficiently strongly upon diffusive encounter to undergo electron-spin exchange, which can be described by an electronic exchange integral, J. Similar interactions occur in solutions of free radicals and in biradicals,[29] and in these cases it is known that J becomes quite small when the two electron spins are separated by more than 10–15 Å.[30] Thus, the quenching process probably operates only when the triplet is in close proximity to a molecule of DTBN; similar behavior may be inferred from studies of triplet quenching by nitric oxide in rigid media.[6c]

The process may be examined in more detail by replacing reaction 8 in the kinetic scheme by reactions 24–26.

$$^3\mathrm{H} + \mathrm{N} \xrightarrow{k_{ex}} \mathrm{C}^* \tag{24}$$

$$\mathrm{C}^* \xrightarrow{k_s} {}^3\mathrm{H} + \mathrm{N} \tag{25}$$

$$\mathrm{C}^* \xrightarrow{k_r} \mathrm{H} + \mathrm{N} \tag{26}$$

The species C* is written simply to represent the triplet–DTBN system during the period of electron-spin exchange; no assumption is made regarding the stability or lifetime of C*. C* may be merely a transient collision complex having a lifetime of 10^{-11} sec or less,[31] or there may be some degree of stabilization in some cases. By definition, k_{ex} represents the rate constant for the formation of triplet–radical pairs which are capable of undergoing spin exchange, while k_s is the overall rate constant for nonproductive separation of the pair. It should be noted that C* may be formed in either a doublet or a quartet state, with formation of the quartet state favored on statistical grounds by a factor of 2.[14c] The rate constants k_{ex} and k_s thus contain contributions from both states of C*; the rate constant for decay of C* to ground-state molecules, k_r, depends only on the doublet state of C* since the T_1–S_0 radiationless transition becomes spin-allowed only for decay from doublet C*. That is to say, the triplet component of doublet C* can undergo facile intersystem crossing to the ground electronic state since the net angular momentum of C* is conserved *via* the exchange interaction.

Analysis of reactions 8 and 24–26, using the steady-state approximation for ^{3}H and C*, leads to the conclusion that

$$k_q = k_{ex}k_r/(k_s + k_r) \tag{27}$$

or

$$k_q = k_{ex}\gamma \tag{28}$$

where γ is the fraction of C* which decays to the ground state. Conceptually, k_{ex} may be associated with the efficiency of spin exchange between the triplet and DTBN, and γ may be associated with the efficiency of radiationless deactivation of C*. Since energy must be conserved in this process, and since we have concluded that the electronic state of DTBN is not changed, then with the reasonable assumption that the partners comprising C* interact sufficiently weakly that their vibrational modes are uncoupled, it becomes apparent that the excitation energy remains on the triplet component of C* and must be dissipated through vibronic coupling with the environment after the triplet has entered the ground-state electronic manifold. Since vibrational relaxation within a given electronic state occurs within *ca.* 10^{-12} sec in condensed media,[32] it can be seen that γ is effectively a function of the transition probability from the zero vibrational level of the excited triplet state to the upper vibrational levels of the ground-state molecule.[33] The total rate constant for this process has been expressed[33] as eq 29 where β_{el} is the electronic

$$k_{A^* \to B} = \frac{2\pi\beta_{el}^2 \sum_n \langle \Phi_{nB}|\Phi_{0A^*}\rangle^2}{\hbar\alpha} \tag{29}$$

matrix element representing the interaction between the electronic wave functions of the excited state (A*) and the ground state (B); the bracketed term is the Franck–Condon factor connecting the vibrational wave function for the levels of B to which the transition initially occurs (Φ_{nB}) and the vibrational wave function for the zero vibrational level of A* (Φ_{0A^*}); and α represents the average energy of the interaction of the molecular vibrational modes with the environment. In this context, we consider that k_{ex} is reflected in a perturbation of β_{el}, since the exchange process controls the efficiency of intersystem crossing in the triplet. The assumption of weak interaction (no vibrational coupling) in C* implies that the lattice coupling parameter α is unchanged during DTBN quenching, so γ should thus be associated with the Franck–Condon term in eq 29. From this it follows that *for a sufficiently similar series of compounds, to the extent that* k_{ex}, k_s, *and* α *may be assumed to remain constant, the measured rate constants for DTBN quenching,* k_q, *should reflect variations in* k_r *and hence reveal variations in the Franck–Condon factors for the compounds.*

An example of this is provided by the values of k_q measured for naphthalene, naphthalene-d_8, and 1-bromonaphthalene; these values are listed in Table II along with the pertinent parameters for the radiative

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(29) We thank Professor J. Freed for pointing out the similarity of exchange-induced quenching to Heisenberg spin exchange, which is observed in solutions of stable free radicals; see, for instance, M. P. Eastman, R. G. Kooser, M. R. Das, and J. H. Freed, *J. Chem. Phys.*, **51**, 2690 (1969).

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(31) A. M. North, "Collision Theory of Chemical Reactions in Liquids," Methuen, London, 1964.

(32) S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(33) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); (b) G. W. Robinson and R. P. Frosch, *ibid.*, **38**, 1187 (1963); (c) J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Advan. Photochem.*, **7**, 149 (1969).

Table II. Triplet Decay Parameters for Naphthalene Derivatives[a]

Compound	k_p, sec^{-1} [b]	k_t, sec^{-1} [c]	k_q, $M^{-1} sec^{-1}$
Naphthalene	0.044	0.35	6.3×10^8
Naphthalene-d_8	0.041[d]	0.012[e]	3.7×10^8
1-Bromonaphthalene	28	22	5.2×10^8

[a] Values of k_p and k_t refer to rigid media at 77°K, and are taken from N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, Chapter 4. [b] Rate constant for phosphorescent triplet decay. [c] Rate constant for nonradiative triplet decay. [d] Taken from ref 34. [e] Calculated according to the procedure given by Turro (footnote *a*), using data from ref 34.

and nonradiative decay of the triplets alone. It is apparent that the well-known[32–34] effect of deuterium substitution on nonradiative transitions is manifested not only in k_t *but also in* k_q. Since k_{ex} and k_s should be essentially unchanged by deuteration, this must mean that the slow step in the quenching process, k_r, depends strongly on the Franck–Condon factor connecting the excited state and ground state, as argued above. Further, the "normal" value of k_q obtained for 1-bromonaphthalene (in contrast to the greatly enhanced values of k_p and k_t) suggests that the effect of the spin–orbit coupling induced by the heavy atom is effectively "saturated" by the spin-exchange process involved in free-radical quenching. Indeed since, k_q for 1-bromonaphthalene is slightly less than for naphthalene, a bromine perturbation of the Franck–Condon factor analogous to that of deuterium might be inferred; the difference in rates is quite small, however, and cannot be considered to be significant in view of the assumptions involved in the calculation of k_q.

It is apparent from Table I that stilbene and biphenyl are both quenched relatively rapidly by DTBN. In both cases, nonvertical triplets are involved, which have equilibrium geometry corresponding roughly to maxima in the ground-state potential energies.[22,25,26] Since nuclear motion is therefore required in order to reach the stable ground-state geometry, vibronic coupling between the excited state and the ground state is expected to be more efficient than for rigid, planar molecules.[33] This is particularly true for stilbene, since the T_1–S_0 energy gap is very small at the equilibrium geometry of the triplet.[1,22]

Finally, it is of interest that the ketone triplets, benzophenone, biacetyl, and fluorenone, are all quenched appreciably more rapidly than the other sensitizers. This probably results from changes in both k_{ex} and in γ. Clearly, both the electronic matrix elements and the Franck–Condon factors for the ketone triplets will be quite different from those for the hydrocarbon triplets.[35] Further, since nitroxides are known to be weak bases which are capable of hydrogen bonding and weak π-complex formation,[30c,36] there may be a tendency for DTBN to associate more closely wth ketone n–π^* triplets than with π–π^* triplets. This would tend to increase k_{ex}, with no obvious countereffect on γ, and thus increase the observed value of k_q. It is particularly noteworthy that fluorenone is quenched substantially more rapidly than 3-acetylphenanthrene. While both ketones have π–π^* lowest triplet states,[37a–c] and 3-acetylphenanthrene clearly behaves like the other aromatic hydrocarbon triplets, the fact that fluorenone is quenched essentially as rapidly as benzophenone suggests that in this case the state being quenched has at least partial n–π^* triplet character. It has been suggested that the n–π^* triplet state of substituted acetophenones lies sufficiently close (*ca.* 3 kcal/mol) to the lower π–π^* state to permit rapid thermal equilibration of the two states prior to photoreaction.[37d] Since the n–π^* state of fluorenone lies quite close to the π–π^* state,[37b,c] it may be that thermal equilibration occurs in this case also, with DTBN quenching occurring predominantly from the upper n–π^* state.

The possibility of a ground-state complex between these ketones and DTBN would of course vitiate these conclusions. The absorption spectrum of fluorenone–DTBN mixtures in the 3300–5000-Å region is the sum of the spectra of the two taken separately. A similar check using benzophenone afforded a similar result. In both cases, DTBN concentrations were comparable to those used in the photochemical experiments. We conclude that a complex is unlikely in these cases. We have no direct evidence in the case of biacetyl, but we see no reason for it to complex with DTBN if the other two ketones do not.

Nature of C*. No evidence for ground-state complexing between DTBN and stilbene or benzophenone at concentrations comparable to or higher than those used in the quenching experiments could be found by ir, uv, or nmr spectroscopy; this is in keeping with other evidence[36c] that the ground-state interactions of DTBN with aromatic hydrocarbons are quite weak. The observations that k_q is in general less than the diffusion-controlled value indicates that some encounters are not effective in relaxing the triplet. This argues against the presence of a (relatively) long-lived complex of DTBN with the excited triplet. Further evidence is provided by a consideration of the effect of DTBN on the benzophenone-sensitized photostationary states of stilbene and β-methylstyrene (β-MS).[1] Since it is known[22a,b,25] that more *cis*-stilbene is formed at photostationary state as the sensitizer triplet energy is lowered from that of benzophenone, a plausible interpretation of the data presented in Figure 1 might have been that energy transfer to stilbene occurred from an exciplex of DTBN and benzophenone triplet having an effective energy of *ca.* 61 kcal/mol.[25] That this is not the case was shown by experiments in which *trans*-β-MS was substituted for the stilbene. Other work in this laboratory[38] has shown that the sensitized photostationary state of β-MS rapidly becomes cis rich as the sensitizer triplet energy is decreased below *ca.* 70 kcal/mol; thus, formation of a benzophenone–DTBN exciplex having E_{C^*} = 61 kcal/mol would be expected[38] to produce a photostationary state consisting of >80% *cis*-β-MS. In fact, as Table III shows, no change at all was observed in the presence of 0.08 *M* DTBN. The contrast between stilbene and

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(34) Reference 8b, Chapter 6.

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Table III. Photostationary State Composition of β-MS[a]

Quencher	[Quencher], M	% *cis*-β-MS[b]
None		62.2
DTBN	0.080	62.1
Azulene	0.010	62.5

[a] Irradiation at 366 nm of degassed benzene solutions containing 0.025 M *trans*-β-MS and 0.050 M benzophenone. [b] Estimated error, ±0.5%.

β-MS is emphasized by the effect of added azulene, which is known[22] to quench stilbene triplets exclusively to *trans*-stilbene at a diffusion-controlled rate. While 0.010 M azulene was sufficient to reduce the stilbene photostationary state composition from 59.5% cis to 36.8% cis,[1] the same concentration produced no detectable effect on the photostationary state of β-MS. Thus, since (1) the photostationary state composition of β-MS is apparently not affected by quenching, and (2) the change in photostationary state expected for sensitization by a low-energy exciplex is not observed, we conclude that C^* *must either dissociate or relax to ground-state molecules before it can be quenched by energy transfer to other species.* The lack of any effect of DTBN or azulene on the photostationary state of β-MS may simply indicate that β-MS triplets are too short-lived to be quenched, or that β-MS triplets are quenched by DTBN without any perturbation of the normal decay ratio.[39] Our data do not permit these possibilities to be distinguished.

Conclusions

The evidence presented here demonstrates that DTBN quenches triplets quite rapidly by exchange-induced vibrational relaxation, and that in this regard the behavior of DTBN is closely analogous to that of nitric oxide. Unless competitive absorption of light becomes a serious problem, DTBN appears to be preferable to NO because of its ease of handling (at least in condensed media). The results with stilbene indicate that DTBN quenching provides a potentially quite useful means of studying triplets which are inaccessible by energy transfer quenching; however, as the result with β-MS suggests, analysis of photostationary states may not be the method of choice for such experiments. It may be possible, for instance, to measure the lifetimes of such nonvertical triplets directly *via* DTBN quenching.

Further, as Table II suggests, DTBN quenching studies can provide unique insight into the relative effects of substituents on the Franck–Condon factors for sufficiently similar molecules, and may thus be of value in interpreting the effects of heavy-atom substituents.[40] Also, if the suggested rationale for the rapid quenching of fluorenone is at all valid, it may well be possible to use DTBN quenching to distinguish between n–π^* and π–π^* triplet states. Finally, it should be possible to investigate the effect of varying the structure of the radical (and therefore of varying k_{ex} and k_s) on the quenching of a given sensitizer triplet by using our approach. In this regard, it should be pointed out that while in our studies no dark reactions occurred and loss of DTBN to side reactions was negligible,[41] the known reactivity of nitroxides as scavengers of transient free radicals[16,30c] demands that systems be studied which do not produce intermediate free radicals.

Experimental Section

Materials. Di-*tert*-butyl nitroxide was prepared by the procedure of Hoffman and coworkers,[20] and gave extinction coefficients at 238 and 465 nm in excellent agreement with reported values. Benzophenone (Fisher "Certified") was recrystallized from hexane, from ether, and again from hexane, and was stored *in vacuo* in an amber bottle, mp 48.5–49.0°. Aldrich *trans*-stilbene was sublimed *in vacuo*, recrystallized twice from absolute EtOH, and again vacuum-sublimed. It too was stored *in vacuo* in an amber bottle; mp 123.5–124.0°. Aldrich *cis*-stilbene was chromatographed on Woelm Activity I neutral alumina with pentane elution. The colorless material was then vacuum distilled after removal of solvent; bp 87–88° (0.4 mm). Other sensitizers were similarly purified prior to use with the exception of perdeuterionaphthalene, which was obtained from Diaprep, Inc., in purity satisfactory for direct use. Aldrich *trans*-β-methylstyrene (containing a small amount of cis isomer) was used as obtained. Reagent grade benzene was carefully purified by selective photochlorination of hydrocarbon impurities,[42] followed by chromatography on Woelm Activity I neutral alumina and two distillations from P_2O_5 through a 4 ft × 0.75 in. column filled with Podbielniak random packing.

Quantum Yield Measurements. Stock solutions of *trans*-stilbene (or *trans*-β-methylstyrene), sensitizers, and DTBN were prepared under red light and transferred to 13 mm o.d. Pyrex ampoules equipped with grease traps[22g] *via* a calibrated syringe. The samples were degassed on a high vacuum line by several freeze–thaw cycles, and were sealed off with a hand torch. Irradiations were carried out at 27° using a Hanovia 450-W mercury arc lamp and Corning narrow-band 366-nm filters in a merry-go-round apparatus[43] immersed in a water bath. Samples irradiated for 10 min typically gave 4–12% conversion to the isomeric olefin, depending on the concentration of DTBN. Actinometry was by the potassium ferrioxalate method,[44] using 0.006 M ferrioxalate solutions; the use of 8-mm windows in the merry-go-round sample compartments eliminated the need to correct the quantum yields for differences in light refraction by the benzene (or cyclohexane) solutions and the aqueous actinometer solution.[45]

Stilbene analysis was by vpc, using an 8 ft × 0.25 in. column of 10% Apiezon J on Anachrom ABS at 230° in an F & M Model 700 research chromatograph with thermal conductivity detector.

Under the conditions used in sample handling and analysis, both the thermal cis–trans isomerization[46] and any isomerization induced by DTBN were negligible. The observed per cent conversion to *cis*-stilbene was corrected for back reaction by the procedure of Lamola and Hammond,[23a] using the appropriate stilbene decay ratio as determined from Figure 1. The vpc analyses were typically reproducible to better than ±0.3% in the comparison of the mean value of replicate samples and to *ca.* ±0.5% for the average devia-

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(39) Since the triplet energy of azulene lies between 31 and 39 kcal/mol,[25] it should be an inefficient quencher of twisted "nonvertical" olefin triplets for which a very small energy gap exists between the triplet state and the ground state at the equilibrium geometry of the triplet. This same condition should make exchange-induced quenching by DTBN quite favorable, so in this case the observed photostationary state will reflect the way the olefin component of C^* decays to its ground state.[1]

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(41) Some loss of DTBN, typically a 2–5% decrease in the concentration of DTBN as monitored by its absorbance at 465 nm,[20] was noted in photostationary state experiments using long irradiation times. The loss of DTBN in quantum yield experiments (typically, irradiation for 10 min) was negligible.

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tion from the mean for replicate injections of the same sample. Typical values of Φ_{TC} (for example, for the quenching of naphthalene triplets) ranged from 0.55 ([DTBN] = 0.0) to 0.36 ([DTBN] = 0.02 *M*) while the corresponding values of f_{HTC} varied from 0.55 to 0.38.

Photostationary State Measurements. Samples prepared and degassed as above were irradiated either in the apparatus as described or in stationary sample holders having 8-mm windows which fit between the filters and the rotating sample carriage of the apparatus; the use of the stationary sample holders increased the light intensity at the sample by about a factor of 3. Photostationary states were reached after irradiation for *ca.* 24–74 hr, depending on the concentration of DTBN used. Samples containing stilbene were analyzed as above. Analysis of the β-methylstyrenes was also by vpc, using a 6 ft × 0.25 in. column of 6% polyphenyl ether on Anachrom ABS at 125°. Selected samples were tested for loss of DTBN to side reactions by monitoring the absorbance of the DTBN at 465 nm[20] with a Cary 14 spectrophotometer before and after irradiation.[41]

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Comments on the Pyrolysis Kinetics of Oxygen Difluoride

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Abstract: The validity of conclusions reached using data obtained from a shock tube kinetic study of the pyrolysis of OF_2 is discussed and the assertion that the differences between shock tube and conventional flow and static system results for this reaction are due to surface effects is examined.

The objective of this publication is to critically review the treatment of the shock tube data made by Lin and Bauer in their reported[1] kinetic study of the pyrolysis of OF_2 and to discuss the validity of their assertion that for this reaction the differences in the kinetic results obtained in conventional static or flow systems are due primarily to surface effects.

Considering the latter point first, it is agreed that investigators of reaction rates using conventional systems must be cautious of the possibility of surface contributions, while shock tube studies are relatively free of this complication. However, if the results from the two types of studies do not agree, it is believed that the conventional system results should not be automatically discounted without additional evidence that the surface contributions are significant. There are numerous examples in the literature in which surfaces have been rendered relatively unreactive, for example: the carbonizing of glass reactor walls during the pyrolysis of pentachloroethane[2] allowed the study of the homogeneous reaction, as evidenced by a change in the surface area/volume ratio of about a factor of 10; or in the case of fluorine containing compounds, the passivating of monel reactor walls essentially eliminated the heterogeneous reaction in the pyrolysis of poly(difluoroamino)fluoromethanes[3] as shown by a change in the surface area/volume ratio of a factor of 8 and by comparing rates obtained from uncoated and Teflon coated reactors.

Specifically, the evidence as to the homogeneity of the OF_2 pyrolysis appears reasonably conclusive because of the following observations.

(a) All of the conventional studies used different reactor materials, aluminum,[4] nickel,[5] monel,[6] and magnesium and several types of glass.[7] It appears extremely unlikely that all of these surfaces would quantitatively affect the pyrolysis rate the same. However, the rates from these static and flow system studies are fairly consistent.

(b) Two studies did increase the surface area of the aluminum and monel reactors by factors of 2 and 2.5, respectively; again no significant change in the rate was observed. It is realized that larger changes in surface area are desirable (in the case of the monel reactor it was not possible); however, this observation when coupled with those described in (a) and (c) strengthens the conclusion that the reaction is homogeneous in conventional systems. In addition, it is acknowledged that a surface may change the rates of both initiation and termination steps such that the overall reaction rate is apparently unaffected by the surface, but it is believed that this situation is the exception rather than the rule for surface reactions.

(c) Generally, surface reactions have lower activation energies than the corresponding homogeneous reactions.[8] Thus, when heterogeneous and homogeneous reactions compete, surface contributions are expected to be relatively lower at higher temperatures. Comparison of the rate constants (Figure 1 of ref 1) and including those obtained in the most recent flow study[6] shows that the accumulated data obtained from all of the conventional systems run about parallel in an Arrhenius plot to that obtained by Lin and Bauer using

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