

QUENCHING OF THE PHOTOCHEMICAL DECOMPOSITION OF n-BUTYRALDEHYDE IN THE VAPOUR PHASE AND IN ISOCTANE

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Summary

The effects of a variety of excited state quenchers on the four major photochemical reaction modes of n-butyraldehyde in the vapour phase and in isooctane have been studied by monitoring primary reactions through the determination of characteristic product quantum yields. Singlet state and triplet state contributions to these photochemical processes were obtained from the quenching plots. Thus it was shown that in the vapour phase 50% of type (II) decomposition occurred from the excited singlet state whereas in isooctane only 20% of type (II) decomposition followed this route. Triplet state lifetimes of 3×10^{-7} s in the vapour phase and 5×10^{-7} s in solution were derived from a kinetic analysis of the quenching data. It was shown that singlet energy transfer to *cis*-piperylene occurred with high efficiency, the rate constants being close to the collision-controlled limit in the vapour phase and to the diffusion-controlled limit in solution.

1. Introduction

In contrast to the simple ketones, little quantitative information is available on the role, lifetimes and reactivities of the excited state precursors involved in the primary photochemical processes of aliphatic aldehydes. Most of the results reported on the singlet and triplet state contribution to the photochemical decomposition of n-butyraldehyde are of a qualitative nature.

Investigation of the quenching of butyraldehyde photolysis by biacetyl [1] and a study of the photosensitization of n-butyraldehyde decomposition by acetone [2] have demonstrated the role played by the triplet state in the vapour phase photolysis. Triplet contribution to type (I) and type (II) decomposition was also confirmed by Cundall and Davies [3] who investi-

gated the effect of *cis*-butene-2 and biacetyl additives. However, the role of the excited singlet state in the vapour phase photolysis has not been elucidated. Singlet state lifetimes were obtained by the single-photon counting technique [4].

Coyle [5] found that part of the reaction was efficiently quenched in benzene solution by penta-1,3-diene and part was relatively unaffected; this indicates that the reaction occurs to an appreciable extent from both the $n\pi^*$ triplet and $n\pi^*$ singlet states in solution. From the quenching constant, a triplet state lifetime of 3.5×10^{-8} s was estimated. Similar conclusions were drawn from the investigations of Lebourgeois *et al.* [6]. Recently, Dalton *et al.* [7] investigated the fluorescence quantum yields and the fluorescence lifetimes of aliphatic aldehydes in hexane. A fluorescence lifetime of 1.7×10^{-9} s was obtained by the single-photon counting technique which is considerably longer than the singlet lifetime reported by Lebourgeois *et al.*

Förgeteg *et al.* [8] have shown that seven primary photochemical processes occur in the photolysis of *n*-butyraldehyde among which the major ones are



A detailed knowledge of the secondary photochemical processes occurring in the vapour phase [8, 9] and in isooctane [8, 10] allows us to obtain detailed information on the singlet and triplet state contribution to all these major primary processes and to determine the excited state lifetimes. Preliminary results obtained with *cis*-piperylene at relatively low quencher concentrations have been published [11]. In this paper we report our results obtained with various quenchers in a broad range of concentration.

2. Experimental

2.1. Technique

A detailed description of the apparatus, method and analysis has been given in a previous publication [11].

In the vapour phase experiments, irradiation of the thoroughly degassed butyraldehyde sample was carried out with an intensity stabilized parallel light beam from an Osram HBO-500 super pressure mercury arc on a conventional optical line. A band (3 nm width) in the 313 nm region was isolated using a combination of NiSO_4 - CoSO_4 - K_2CrO_4 - $\text{KHC}_8\text{H}_4\text{O}_4$ solution and UG 11 (Schott, Jena) glass filters. The reaction was carried out in a cylindri-

cal quartz cell of internal diameter 4.5 cm and length 8.0 cm equipped with Ultrasil planparallel windows.

In the solution experiments, a series of samples with varying quencher concentration were prepared in cylindrical UVIOL cuvettes (internal diameter 1.2 cm) and were irradiated simultaneously. Two methods were used. In one, the cuvettes were mounted on a rotating holder drum and were irradiated with the light beam obtained from an optical line similar to that used in the vapour phase experiments. In the rest of the experiments a rotating 125 W Philips medium pressure arc, surrounded by the sample cuvettes, was used as a light source. A filter solution ($\text{NiSO}_4\text{-CoSO}_4\text{-KHC}_8\text{H}_4\text{O}_4$) isolating a band in the 313 nm region was circulated through the filter jacket surrounding the arc.

After irradiation, samples were separated into gas and condensable fractions. Both were analysed by gas chromatography using internal standards. Altogether four columns were required to determine the composition of the irradiated samples [11].

2.2. Materials

n-Butyraldehyde (Fluka, Puriss) was purified by precipitation with sodium hydrogen sulphite. The aldehyde was recovered with a dilute solution of NaHCO_3 , dried and further purified by distillation *in vacuo*. The purified sample contained about 0.5% isobutyraldehyde.

The quenchers used were as follows: *cis*-piperylene (Fluka, pure), *cis*-butene-2 (Fluka, pure), biacetyl (Reanal, Puriss). They were purified by atmospheric distillation or sublimation and bulb-to-bulb distillation *in vacuo*. The middle fractions were retained for use.

The isooctane (Fluka, pure) solvent, the isopentane (Koch-Light, Puriss) and cyclohexanone (Reanal, Puriss) internal standards were distilled on a high performance column and further purified by bulb-to-bulb distillation *in vacuo*. The middle third fractions were retained for use.

3. Results and discussion

3.1. Characterization of primary photochemical processes

The determination of the singlet and triplet state contributions to the primary photochemical processes as well as the analysis of the quenching data by the Stern-Volmer treatment require the knowledge of the relative primary quantum yields ϕ_0/ϕ , *i.e.* the ratio of the primary quantum yields in the absence and presence of the quencher, as a function of quencher concentration. For primary reactions (II) and (II'), the required information can be obtained in a straightforward manner by measuring directly the quantum yields for the primary products. However, this is not the case for reactions (I) and (IV) which yield free radicals. Apart from the physical quenching effect (energy transfer), the quenchers may react with the free radicals thereby causing chemical quenching as well. This alters the stoichiometry of the

reaction and shortens the reaction chains if any are involved in product formation. As a result, the characterization of primary processes (I) and (IV) requires a careful consideration of the reaction kinetics and mechanism.

It is known that $C_3H_7\dot{C}HO^*$ can decompose directly into C_3H_8 and CO which are identical with the major final products of primary reaction (I). However, since the quantum yield of direct decomposition is small at 313 nm (about 0.015 [12]) compared with the quantum yield of \dot{C}_3H_7 and $\dot{C}HO$ formation we can simply neglect the direct reaction in the estimation of the type (I) quantum yields from the product yields determined at 313 nm wavelength.

Reaction chains are involved in the formation of the products of secondary reactions following type (I) decomposition both in the vapour phase [9] and in solution [10]. However, chain length is small at low temperatures and low aldehyde concentrations. Thus, the results presented later were all obtained at room temperature and at aldehyde concentrations of 2.7×10^{-3} mol dm⁻³ in the vapour phase and 1.0×10^{-2} mol dm⁻³ in isooctane.

On considering the product distribution [8] and the fate of the $\dot{C}HO$ and \dot{C}_3H_7 radicals in the vapour phase [9] and in isooctane [10], we assume that quenching of type (I) decomposition can be monitored by determining the quantum yields for CO or the weighted sum of quantum yields for $C_3H_8 + 2C_6H_{14} + C_3H_6$. Furthermore, we can characterize reaction (IV) by the yields for heptanol-4 + n-butanol which are the only significant products formed from the $C_3H_7\dot{C}HOH$ free radical [9, 10].

These product yields are termed "characteristic product yields" and are used later in the presentation of the quenching results for reactions (I) and (IV).

3.2. Singlet and triplet contribution to the primary processes

In order to obtain reliable results for the singlet and triplet state contributions to the individual primary processes, various quenchers were added. Thus, we used *cis*-piperylene (3×10^{-5} – 2×10^{-2} mol dm⁻³), biacetyl (1×10^{-5} – 6×10^{-4} mol dm⁻³) and *cis*-butene-2 (9×10^{-4} – 4×10^{-2} mol dm⁻³) in the vapour phase, and *cis*-piperylene (1×10^{-4} – 3.5 mol dm⁻³) and naphthalene (2×10^{-4} – 2×10^{-2} mol dm⁻³) in isooctane.

Quenching of type (II) decomposition in the vapour phase by piperylene is shown in Fig. 1. Efficient quenching by piperylene at quencher concentrations below 1×10^{-4} mol dm⁻³ and a much less efficient quenching at high concentrations is apparent. Assuming that the former is caused by triplet energy transfer while the latter is due to singlet energy transfer, we estimate ${}^1\eta = 0.50$ and ${}^3\eta = 0.50$ respectively for the singlet and triplet contribution to type (II) decomposition in the vapour phase. (Here and later ${}^1\eta = {}^1\phi_0 / ({}^1\phi_0 + {}^3\phi_0)$ and ${}^3\eta = {}^3\phi_0 / ({}^1\phi_0 + {}^3\phi_0)$ designate the proportions of the singlet and triplet state contributions to the primary process in question in the absence of quenchers). For reactions (II) and (II'), ${}^1\eta$ and ${}^3\eta$ were simply obtained by back-extrapolation of the second, linear portion of the quenching

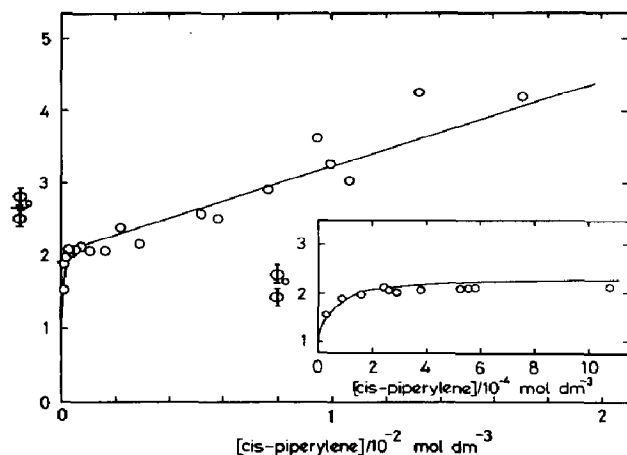


Fig. 1. Stern-Volmer plot for quenching of type (II) decomposition by *cis*-piperylene in the vapour phase: \circ , CH_3CHO .

(Φ/Φ_0 versus $[Q]$) or Stern-Volmer plots. However, in the case of reactions (I) and (IV) where chemical quenching (radical scavenging) occurred in addition to physical quenching in the presence of quenchers, $^1\eta$ and $^3\eta$ were estimated from a comparison of the Φ/Φ_0 values obtained with different quenchers at sufficiently high quencher concentrations. As with *cis*-piperylene, biacetyl was found to quench type (II) decomposition efficiently from the triplet state. Limiting values for the C_2H_4 and CH_3CHO quantum yields were apparently approached at around $7 \times 10^{-5} \text{ mol dm}^{-3}$ biacetyl concentration which corresponds to 50% singlet contribution, in excellent agreement with the piperylene results. Singlet state quenching was not observed in the biacetyl concentration range used. Butene-2 was shown to quench type (II) decomposition from the triplet state less efficiently than the other compounds. Complete quenching of the triplet reaction could only be approached with 680 Torr of butene-2, the highest quencher concentration used.

Quenching of type (II) decomposition in isooctane by *cis*-piperylene is shown in Fig. 2. A comparison with the vapour phase results (see Fig. 1) shows that quenching of type (II) decomposition is more extensive in isooctane, indicating singlet and triplet state contributions $^1\eta = 0.25$ and $^3\eta = 0.75$ respectively. Results obtained with naphthalene as quencher were similar, namely $^1\eta = 0.20$ and $^3\eta = 0.80$.

Quenching of cyclobutanol formation in the vapour phase by *cis*-piperylene, biacetyl and *cis*-butene-2 revealed that 80% of the reaction occurred from the triplet state and 20% from the excited singlet state. The quencher concentrations required to suppress the triplet reaction were found to be the same as in the case of the type (II) reaction. Quenching in isooctane by naphthalene and *cis*-piperylene gave $^1\eta = 0.05\text{--}0.15$ and $^3\eta = 0.95\text{--}0.85$. The Stern-Volmer plot for quenching of type (II') reaction by naphthalene is shown in Fig. 3.

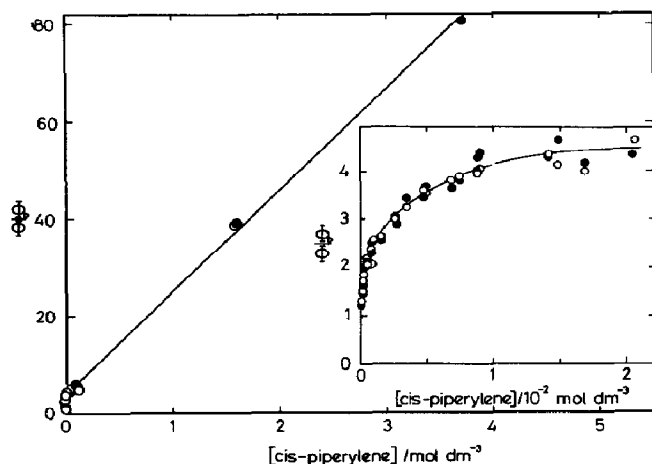


Fig. 2. Stern-Volmer plot for quenching of type (II) decomposition by *cis*-piperylene in isooctane: ●, C_2H_4 ; ○, CH_3CHO .

Quenching of type (I) decomposition in the vapour phase by *cis*-piperylene is demonstrated in Fig. 4. The results indicate that at least 80% of type (I) decomposition is quenched efficiently by piperylene. The shape of the Stern-Volmer plot indicates the occurrence of efficient free radical trapping by piperylene. Reaction between piperylene and the free radicals formed in type (I) decomposition may be responsible for the upward curvature of the characteristic type (I) product quantum yields. (Note the difference in the increase of the CO and the $C_3H_8 + 2C_6H_{14} + C_3H_6$ ratios which is caused by less efficient trapping of $\dot{C}HO$ than \dot{C}_3H_7 .) However, the results obtained with the less reactive *cis*-butene-2 (Fig. 5) seem to indicate that quenching by piperylene was caused for the most part by energy transfer

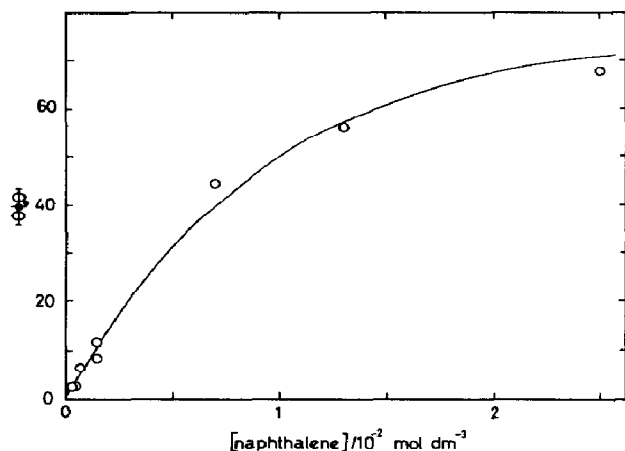


Fig. 3. Stern-Volmer plot for quenching of cyclobutanol formation by naphthalene in isooctane.

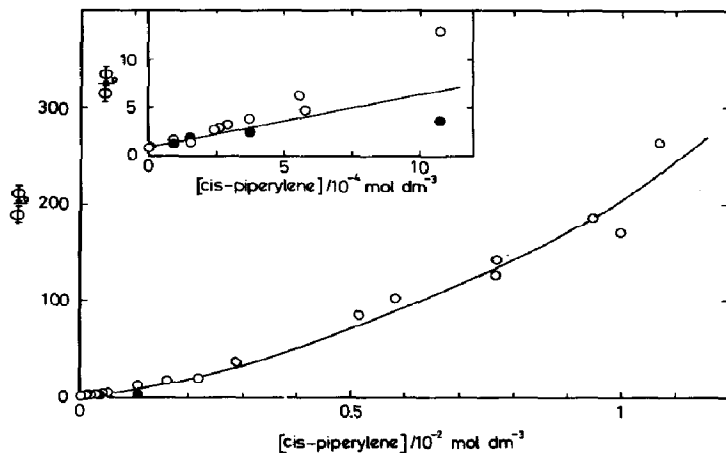


Fig. 4. Stern-Volmer plot for quenching of type (I) decomposition by *cis*-piperylene in the vapour phase: ●, CO; ○, $C_3H_8 + 2C_6H_{14} + C_3H_6$.

and that the singlet and triplet contributions are around $^1\eta = 0.2$ and $^3\eta = 0.8$. We have attempted to investigate the quenching of type (I) product formation by biacetyl. Only slight quenching was found, in accordance with the observations of Borkowski and Ausloos [1]. These authors considered this to be an indication that type (I) dissociation occurs from a singlet electronic state and/or from a triplet electronic state excited to a high vibrational level. In the light of our piperylene and butene-2 quenching results we prefer to explain the apparent inefficiency of biacetyl by the occurrence of *n*-butyraldehyde decomposition photosensitized by biacetyl which partly compensates the deactivation of the triplet state of the aldehyde.

Quenching of type (I) decomposition in isooctane by *cis*-piperylene and naphthalene is shown in Figs. 6 and 7 respectively. The results clearly

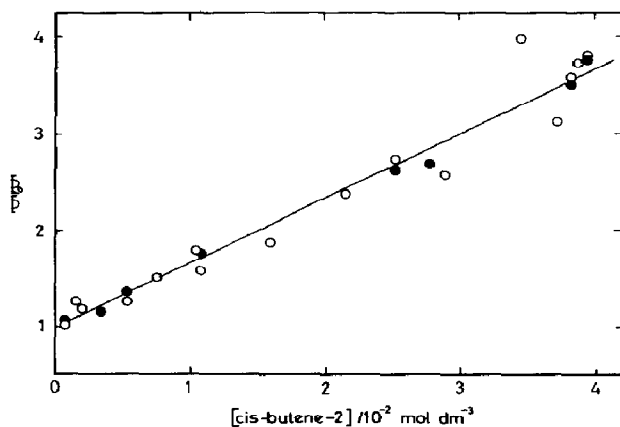


Fig. 5. Stern-Volmer plot for quenching of type (I) decomposition by *cis*-butene-2 in the vapour phase: ●, CO; ○, $C_3H_8 + 2C_6H_{14} + C_3H_6$.

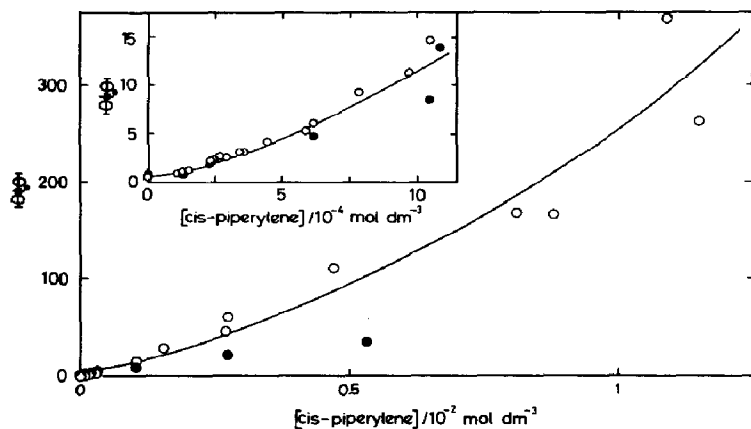


Fig. 6. Stern-Volmer plot for quenching of type (I) decomposition by *cis*-piperylene in isooctane: ●, CO; ○, $C_3H_8 + 2C_6H_{14} + C_3H_6$.

indicate that type (I) decomposition occurs from the triplet state in solution, *i.e.* $^1\eta = 0.05$ and $^3\eta = 0.95$.

Photoreduction reaction (IV) was practically entirely quenched by *cis*-piperylene and biacetyl in the vapour phase and by *cis*-piperylene and naphthalene in isooctane, *i.e.* $^1\eta \approx 0$ and $^3\eta \approx 1.0$. Quenching by naphthalene in isooctane is shown in Fig. 8.

A summary of excited singlet and triplet state contributions to the major primary processes of *n*-butyraldehyde photolysis is given in Table 1. In accordance with the higher triplet yield in isooctane [13], the role of the triplet state is seen to be more important in solution than in the vapour phase.

3.3. Quenching constants and excited state lifetimes

In order to obtain the quenching constants $K_Q = k_Q\tau_0$, plots of the relative characteristic product yields Φ_0/Φ versus $[Q]$ were examined. For

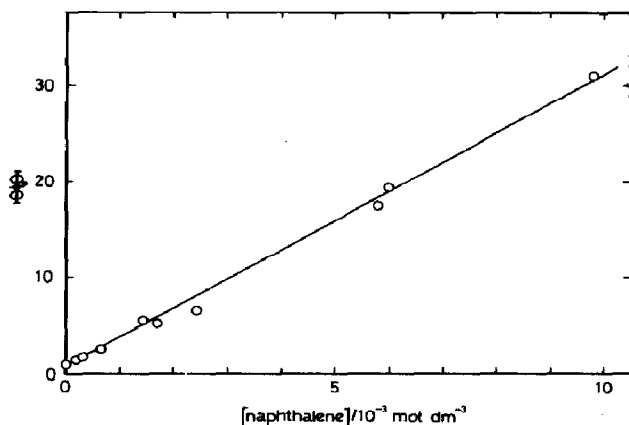


Fig. 7. Stern-Volmer plot for quenching of type (I) decomposition by naphthalene in isooctane. ○, $C_3H_8 + 2C_6H_{14} + C_3H_6$.

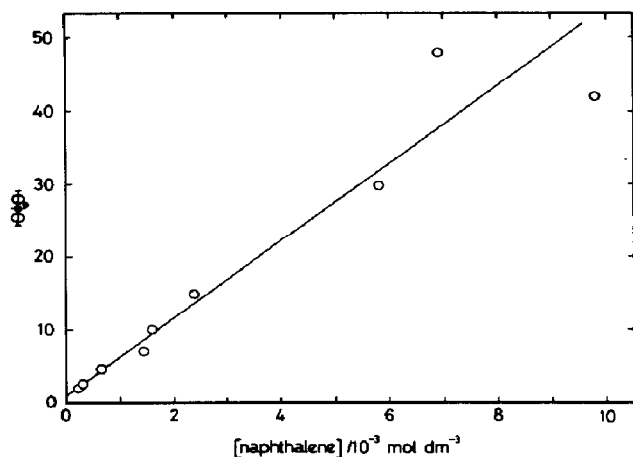


Fig. 8. Stern–Volmer plot for quenching of characteristic products of reaction (IV) by naphthalene in isooctane: \circ , heptanol-4 + n-butanol.

type (II) and (II') processes the Φ_0/Φ versus $[Q]$ plots were bent towards the $[Q]$ axis, as expected for photochemical processes occurring from two excited states with ${}^3K_Q > {}^1K_Q$ [14]. In the case of *cis*-piperylene quenching where quencher concentrations were extended to high values which caused significant singlet state quenching, the curve approached an oblique asymptote at high piperylene concentrations. This can be seen for instance in Fig. 2. where a Stern–Volmer plot for quenching of reaction (II) by piperylene in isooctane is presented. Kinetic analyses for photochemical reactions that involve quenching of two excited states have been published [14 - 17]. Here we interpret our results using the simple treatment given by Dalton and Turro [14]. They have shown that, assuming an irreversible singlet \longrightarrow triplet transition, the initial slope (IS) and the slope of the oblique asymptote (SOA) can be expressed as

TABLE 1

Singlet and triplet contributions to the major reaction paths

Primary process		${}^1\eta$	${}^3\eta$
(I)	gas phase	0.2	0.8
	solution	0.05	0.95
(II)	gas phase	0.50	0.50
	solution	0.20–0.25	0.80–0.75
(II')	gas phase	0.20	0.80
	solution	0.05–0.15	0.95–0.85
(IV)	gas phase	0	1.0
	solution	0	1.0

$$IS = {}^1K_Q + {}^3\eta {}^3K_Q \quad (1)$$

$$SOA = \frac{1}{{}^1\eta} {}^1K_Q \quad (2)$$

where ${}^1\eta = {}^1\phi_0/({}^1\phi_0 + {}^3\phi_0)$ and ${}^3\eta = {}^3\phi_0/({}^1\phi_0 + {}^3\phi_0)$ are the singlet and triplet contributions, respectively, to the primary process in the absence of quencher, while ${}^1K_Q = {}^1k_Q {}^1\tau_0$ and ${}^3K_Q = {}^3k_Q {}^3\tau_0$ are the singlet and triplet quenching constants respectively. Since values for ${}^1\eta$ and ${}^3\eta$ could be taken from Table 1, the initial slopes supplied 3K_Q (note that ${}^3\eta {}^3K_Q \gg {}^1K_Q$) and the slopes for the oblique asymptotes were used to derive 1K_Q .

For reactions (I) and (IV), the Φ_0/Φ versus $[Q]$ plots obtained with piperylene quencher were bent upwards as shown in Fig. 6 where the Stern-Volmer plot for quenching of type (I) decomposition by *cis*-piperylene in isooctane is depicted. The upward curvature is an indication of chemical quenching (rather than quenching of two reactive excited states with ${}^1K_Q > {}^3K_Q$), which is a result of trapping of \dot{C}_3H_7 and $\dot{C}HO$ radicals by the conjugated diolefin. (Less efficient trapping of $\dot{C}HO$ compared with that of \dot{C}_3H_7 causes less curvature in the CO data than in the $C_3H_8 + 2C_6H_{14} + C_3H_6$ results.) This is supported by the fact that the rest of the quenchers which are much less reactive than piperylene towards free radicals showed no upward curvature. As an example we refer to the Stern-Volmer plot for type (I) quenching by naphthalene in isooctane shown in Fig. 7. The Φ_0/Φ versus $[Q]$ data determine a straight line as expected on the basis of the chemical inertness of naphthalene and from the negligible contribution of the excited singlet state to type (I) decomposition.

Triplet state quenching constants for a given quencher were obtained from the initial slopes of the Stern-Volmer plots of all four primary reactions. The average values are given in Table 2. Agreement between the 3K_Q values obtained from the quenching data for different reactions was generally satisfactory as can be seen from the error limits which were intended to cover the individual 3K_Q determinations. Larger differences were observed only in isooctane with piperylene and naphthalene quenchers where the 3K_Q values derived from the quenching data for reactions (II') and (IV) were higher by a factor of 1.5–2 than those obtained from monitoring reactions (I) and (II). Since type (I) and (II) decompositions are of greater importance in the photochemistry of *n*-butyraldehyde and could thus be measured with higher accuracy we have omitted the results derived from the quenching plots of reactions (II') and (IV) in isooctane. Thus, the results seem to indicate that the triplet states involved in all the primary reactions studied have lifetimes which differ by less than the limits of experimental error.

Singlet state quenching constants could be obtained in the vapour phase and in isooctane from the data for type (II) quenching by piperylene. The results derived from the slopes of the oblique asymptotes are given in Table 2.

On examining the triplet state quenching parameters obtained in the vapour phase, it can be seen from Table 2 that if biacetyl quenches the butyraldehyde triplet with unit efficiency, the relative values of the rate

TABLE 2

Quenching parameters

Quencher	Vapour phase		Isooctane	
	${}^3K_Q = {}^3k_Q {}^3\tau_0$ (dm ³ mol ⁻¹)	${}^1K_Q = {}^1k_Q {}^1\tau_0$ (dm ³ mol ⁻¹)	${}^3K_Q = {}^3k_Q {}^3\tau_0$ (dm ³ mol ⁻¹)	${}^1K_Q = {}^1k_Q {}^1\tau_0$ (dm ³ mol ⁻¹)
<i>cis</i> -Piperylene	$(8.3 \pm 1.0) \times 10^3$	58	$(4.0 \pm 0.1) \times 10^3$	5.5
Biacetyl	$(4.8 \pm 0.5) \times 10^4$			
<i>cis</i> -Butene-2	76 ± 10			
Naphthalene			$(3.2 \pm 0.1) \times 10^3$	

constants for quenching by biacetyl, piperylene and butene-2 are about 1, $\frac{1}{6}$ and $\frac{1}{600}$ respectively. Triplet energy transfer from n-butyraldehyde to biacetyl is highly exothermic, as estimated from the triplet energies of 78 kcal mol⁻¹ [11] and 54.9 kcal mol⁻¹ [18] for the aldehyde and the diketone respectively. Thus we might expect that the efficiency of energy transfer is not far from unity. Assuming 3K_Q for biacetyl to be equal to the bimolecular rate constant for collision, i.e. ${}^3K_Q = 1.3 \times 10^{-11}$ dm³ mol⁻¹ s⁻¹, ${}^3\tau_0 = 4 \times 10^{-7}$ s is obtained for the lifetime of the reacting triplet state. No comparison can be made with other estimates since triplet lifetimes for butyraldehyde in the vapour phase have not been published.

The similarity of the triplet state quenching parameters for *cis*-piperylene and naphthalene in isooctane is in agreement with the observation of Hammond and Leermakers [19] who found these additives to quench photoreduction of benzophenone with the same efficiency. In view of the exothermicity of triplet energy transfer from butyraldehyde to piperylene and naphthalene we can assume that these processes are diffusion controlled. If we take the viscosity of isooctane at 298 K to be 4.4×10^{-3} P, ${}^3k_Q = k_{\text{diff}} = 1.4 \times 10^{10}$ dm³ mol⁻¹ s⁻¹ according to the Debye equation [20]. With this value for the rate constant of triplet state quenching, the quenching constants of piperylene and naphthalene yield ${}^3\tau_0 = 3 \times 10^{-7}$ s for the lifetime of the reacting triplet state in isooctane. This value is close to the triplet state lifetime obtained in the vapour phase.

Our triplet state lifetime is higher by about one order of magnitude than those reported in the literature. Coyle [5] obtained ${}^3\tau_0 = 3.5 \times 10^{-8}$ s from piperylene quenching experiments in benzene using 0.1–0.2 mol dm⁻³ aldehyde concentrations. Lebourgeois *et al.* [6] reported ${}^3\tau_0 = 3 \times 10^{-8}$ s at 5.6×10^{-2} mol dm⁻³ aldehyde concentration in n-heptane using naphthalene as quencher and monitoring the reaction by determination of the disappearance of the CO group. Both estimates were based on measurements made at higher aldehyde concentrations than the 1×10^{-2} mol dm⁻³ used in the present work.

In a previous paper [10] we have shown that self-quenching occurs in the photolysis of n-butyraldehyde which is detectable even at 1×10^{-3} mol

dm^{-3} aldehyde concentration in isooctane. Thus the measured lifetime ${}^3\tau_0$ is a function of the aldehyde concentration $[A]$:

$${}^3\tau_0 = \frac{{}^3\tau'_0}{1 + {}^3k_{\text{PhR}} {}^3\tau'_0 [A]} \quad (3)$$

where ${}^3\tau'_0$ is the triplet lifetime extrapolated to zero aldehyde concentration (defined as the reciprocal of the sum of rate constants for unimolecular processes of the triplet state) and ${}^3k_{\text{PhR}}$ denotes the bimolecular rate constant for self-quenching (*i.e.* for photoreduction). Using ${}^3k_{\text{PhR}} {}^3\tau'_0 = 73 \pm 28 \text{ dm}^3 \text{ mol}^{-1}$ derived from the kinetic analysis of self-quenching in isooctane [10] and ${}^3\tau_0 = 3 \times 10^{-7} \text{ s}$ obtained in the present study at $1 \times 10^{-2} \text{ mol dm}^{-3}$ aldehyde concentration, a value of ${}^3\tau'_0 = 5 \times 10^{-7} \text{ s}$ is calculated from eqn. (3) for the true triplet state lifetime of butyraldehyde in isooctane. It is easy to show by means of eqn. (3) and the parameters given that an apparent lifetime of $4 \times 10^{-8} \text{ s}$ is expected at 0.15 mol dm^{-3} aldehyde concentration which agrees exactly with the value reported by Coyle [5]. The agreement is not as good, however, with the triplet lifetime reported by Lebourgeois *et al.* [6].

Turning now to the interpretation of the singlet state quenching parameters, a similar procedure to that used for the triplet data does not seem to be warranted. As singlet energy transfer is less exothermic, we expect ${}^1k_{\text{Q}}$ to be smaller than the rate constant for collision or the rate constant for diffusion in the vapour phase and in isooctane respectively. However, fluorescence lifetimes were measured by the single-photon counting technique. Thus the results of Hansen and Lee [21] indicate that the fluorescence decay time is $3.2 \times 10^{-9} \text{ s}$ in the vapour phase at 313 nm and 12 Torr pressure. Assuming that the lifetime is not markedly influenced by the pressure, a bimolecular rate constant for piperylene quenching of ${}^1k_{\text{Q}} = 1.8 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained from the quenching parameter given in Table 2. This is less by a factor of about 7 than the bimolecular rate constant for collision. Dalton *et al.* measured a fluorescence decay time of $1.7 \times 10^{-9} \text{ s}$ in hexane. With the reasonable assumption that lifetimes in hexane and isooctane are similar, a bimolecular rate constant for piperylene quenching in isooctane of ${}^1k_{\text{Q}} = 3.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is obtained from the singlet quenching constant given in Table 2. This is less by a factor of about 4 than the rate constant for diffusion.

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