

## PHOTOCHEMISTRY OF ALIPHATIC ALDEHYDES

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### Summary

The photochemistry of alkanals in dilute solutions and in the presence of olefins and hydrogen donors was analysed and the results obtained are discussed taking as reference the photochemical behaviour of the alkanones.

Intermolecular and intramolecular hydrogen abstraction take place in alkanals and alkanones with similar rates. However, there are differences in their behaviour towards unsaturated compounds that can be related to differences in ionization potentials and electron affinities.

A distinct feature of alkanal photochemistry is the relevance of auto-quenching in both the singlet and triplet states. The singlet lifetimes of the alkanals, when extrapolated to zero alkanal concentration, decrease with  $\alpha$  substitution. The results obtained indicate that this effect is not due to type I photofragmentation.

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### 1. Introduction

The photochemistry of aliphatic aldehydes in solution has been scarcely investigated [1 - 7], and very few studies regarding the relationship between the aldehyde structure and its photochemical reactions have been carried out [1, 5, 6]. The evaluation of rate constants for singlet and triplet photoprocesses is considerably more difficult in the alkanals than in the alkanones. This difficulty is a consequence of the rather large number of possible photo-reactions [4], the occurrence of chain decompositions, the fast autoquenching reactions [2, 4, 5] and the competition between the quenching of singlet and triplet states by di-olefins that makes the selective quenching of the triplet difficult. The fact that some of these factors have been frequently neglected casts doubts on the validity of the reported data for the singlet [2, 6] and triplet photoprocesses in alkanals. In the present work we carried

out a study of the photoprocesses of the singlet states of excited alkanals and we discuss the relevance of these reactions in the evaluation of the rates of excited triplet photoreactions.

## 2. Experimental

The experimental conditions were similar to those described previously [8]. Fluorescence measurements were carried out in a 204-S Hitachi-Perkin-Elmer spectrofluorimeter.

The aldehydes (Fluka) were distilled under vacuum before use and only freshly prepared solutions were employed.

## 3. Results and discussion

The photochemistry of the singlet state of a given alkanal (A) in the presence of a quencher (Q) can be represented by the following reaction scheme:



### 3.1. Autoquenching and singlet lifetime

The slopes SV of the Stern-Volmer plots obtained by plotting the fluorescence intensity at a given concentration of A as a function of Q are given by

$$SV^{-1} = (k_Q\tau_0)^{-1} + (k_A/k_Q)[A] \quad (10)$$

where  $\tau_0$  is the singlet lifetime in the limit of [A] equal to zero. Figure 1 shows the data obtained for *n*-butanal when triethylamine and isoprene are employed as quenchers plotted according to eqn. (10). Since SV is equal to

TABLE 1

Experimental results for the excited singlet with *n*-hexane as solvent

Aldehyde	$k_{\text{autoquenching}}$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )	$(\tau^{\circ})_{\text{S}}$ (ns)	$(k_{\text{II}})_{\text{S}}$ ( $\times 10^8 \text{ s}^{-1}$ )
Propanal	1.3	3.3	—
1-Butanal <sup>a</sup>	2.2 (2.0)	2.5 (2.5)	0.8
1-Pentanal	3.3	1.5	3.6
1-Heptanal <sup>b</sup>	2.4	1.2	5.3
3-Methyl-1-butanal <sup>b</sup>	2.5	2.8	0.5
2-Methylpropanal	2.0	1.9	—
2,2-Dimethylpropanal	0.9	0.8	—

<sup>a</sup>The values in parentheses were obtained employing isoprene as quencher.

<sup>b</sup>The values of  $\tau_{\text{S}}$  at  $[A] = 0.1 \text{ M}$  were obtained from the value reported for butanal [6] and the relative values of the fluorescence quantum yields and the integrated absorption bands.

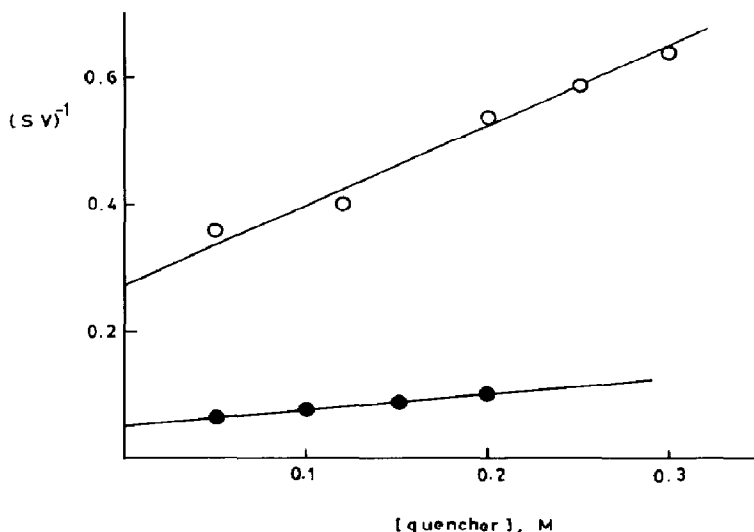


Fig. 1. The dependence of the reciprocal Stern-Volmer constant for the fluorescence quenching of butanal on the quencher concentration of butanal in *n*-hexane (butanal concentration, 0.05 M): ○, isoprene as quencher; ●, triethylamine as quencher.

$k_{\text{Q}}\tau$  (where  $\tau$  is the singlet lifetime at the concentration of A considered), the relationship between the intercept and a given value of  $\text{SV}^{-1}$  is equal to  $\tau/\tau_0$ . The values of  $\tau_0$  obtained from this method employing triethylamine as quencher and the values of  $\tau$  at  $[A] = 0.1 \text{ M}$  reported by Dalton *et al.* [6] are given in Table 1. Furthermore, since

$$\tau^{-1} = \tau_0^{-1} + k_{\text{A}}[A] \quad (11)$$

evaluation of  $\tau_0$  and  $\tau$  allows the determination of  $k_{\text{A}}$ . These values are also included in Table 1. For *n*-butanal,  $\tau_0$  and  $k_{\text{A}}$  were also evaluated using iso-

prene as quencher. The fact that the values obtained are independent of the quencher validates the method employed.

The values of  $k_A$  show very little dependence on the alkanal structure. The fact that 2,2-dimethylpropanal has the lowest value of  $k_A$  could be attributed to steric hindrance, but it has to be considered that the difference between this value and that obtained for propanal is within the experimental error. A treatment similar to that employed in the present work has been reported by Daccord *et al.* [9] for propanal, butanal, hexanal and 2-ethylbutanal using biacetyl as quencher. The values of  $\tau_0$  reported are in substantial agreement with those given in Table 1. However, the values of  $k_A$  are considerably lower than those found in the present work, a result that can reflect differences in the experimental conditions employed. For example, it has been found in the present work that when acetonitrile is employed as solvent the values of  $\tau_0$  are quite close to those obtained in *n*-hexane while the values of  $k_A$  are considerably smaller (at least a factor of 5) than those obtained in *n*-hexane.

The values of  $\tau_0$  show a decrease with both  $\gamma$  and  $\alpha$  substitution. This trend is similar to that reported by Dalton *et al.* [6] from the uncorrected values obtained at a 0.1 M alkanal concentration. Assuming that  $k_{ISC}$  only depends on  $\alpha$  substitution, a comparison between the singlet lifetime of a given A and that of *n*-propanal allows an estimation of  $(k_{II})_S$  in the former compound. The values obtained are included in Table 1. These values are smaller than those reported by Dalton *et al.* [6] because of the autoquenching contribution to the singlet lifetime under the conditions employed in their work.

The values of  $(k_{II})_S$  obtained for *n*-butanal lead to an activation energy of approximately 4 kcal mol<sup>-1</sup>. This value is considerably smaller than that calculated in an MINDO/3 (modified intermediate neglect of differential overlap) study of the reaction carried out by Dewar and Doubleday [10].

### 3.2. Relevance of type I photofragmentations

The decrease in  $\tau_S$  with  $\alpha$  substitution is contrary to the trend observed in the alkanones [11]. This result has led Dalton *et al.* [6] to suggest a significant contribution of type I cleavage to the singlet lifetimes of 2-methylpropanal and 2,2-dimethylpropanal. If the trend in  $k_{ISC}$  in the alkanals is similar to that observed for the alkanones, this suggestion implies that the photocleavage quantum yield  $\phi_I$  must be larger than 0.4 and 0.7 for 2-methylpropanal and 2,2-dimethylpropanal respectively. In order to evaluate  $\phi_I$  in the photolysis of 2-methylpropanal we measured  $\phi_{C_2H_6}$  in the presence of di-*tert*-butylnitroxide and diethylhydroxylamine, and the polymerization rate of styrene photoinitiated by 2-methylpropanal. The  $\phi_{C_2H_6}$  value in the presence of di-*tert*-butylnitroxide (0.0375 M) is less than  $5 \times 10^{-9}$ . This value can be considered as an upper limit for both reaction (7) and cage disproportionation following reaction (6).

Diethylhydroxylamine is a suitable quencher for detecting the production of free radicals from the singlet state because of its efficiency as a

TABLE 2

Quenching rate constants for alkanal singlets by olefins in *n*-hexane solution

Alkanal	Quenching rate constant $k_{\phi}$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )				
	2,5-Dimethyl- hexadiene	<i>cis</i> -1,3- Pentadiene	$\alpha$ -Methyl- styrene	Cyclo- hexene	Dicyano- ethylene
(Ionization potential)	(7.91)	(8.68)	(<8.47) <sup>a</sup>	(8.72)	(11.16)
Propanal	10.7	1.67	1.07	0.7	(1.7) <sup>b</sup>
Butanal	11.0	2.3	1.21	0.7	1.67 (2.3) <sup>b</sup>
Pentanal	8.9	3.4	1.57	1.0	(1.8) <sup>b</sup>
3-Methylbutanal	—	1.6	—	—	—
Heptanal	7.4	3.8	2.21	1.1	—
2-Methylpropanal	8.9	2.1	0.75	0.7	(1.0) <sup>b</sup>
2,2-Dimethylpropanal	18.7	—	2.74	1.2	(1.4) <sup>b</sup>

<sup>a</sup> Value for styrene.<sup>b</sup> From ref. 6 in acetonitrile.

triplet quencher and because of the fact that it reacts quantitatively with isopropyl radicals to produce propane and a stable diethylnitroxide radical [12]. The quantum yield  $\phi_{\text{C}_3\text{H}_7}$  of isopropyl radicals produced by photocleavage from the singlet state, which avoids cage recombination, can be estimated by this method to be less than about 0.05. A similar value for  $\phi_{\text{C}_2\text{H}_5}$  can be evaluated by measuring the initiation efficiency in the photopolymerization of styrene [13]. These low values can only be made compatible with the  $\phi_1$  value required to explain the shorter lifetime of 2-methylpropanal if the photofragmentation is followed by a very efficient cage recombination. Several results make this possibility unlikely: (1) the lack of "cage disproportionation" products observed in the presence of di-*tert*-butylnitroxide; (2) chemically induced dynamic nuclear polarization results indicate that most of the radical pairs produced are of triplet character [14]; (3) in *tert*-butylketones most of the radicals produced from the singlet state avoid cage recombination [15]. An alternative explanation could be an increase in  $\phi_{\text{IC}}$  with  $\alpha$  substitution and there are some experimental data that would indicate that a similar effect could be present in the photolysis of unsymmetrically  $\alpha$ -substituted alkanones. In fact, it has been found that  $\phi_1$  in the gas phase photolysis of 3-methyl-2-butanone is considerably less than unity [16] and that  $\phi_{\text{radicals}}$  in the solution photolysis of 3,3-dimethyl-2-butanone, although considerably less than unity [15], is independent of the solvent viscosity [17].

### 3.3. Singlet quenching by unsaturated compounds

Evidence exists for a photochemical addition of aliphatic aldehydes to alkenes according to the Paterno-Buchi reaction to yield oxetanes in a region

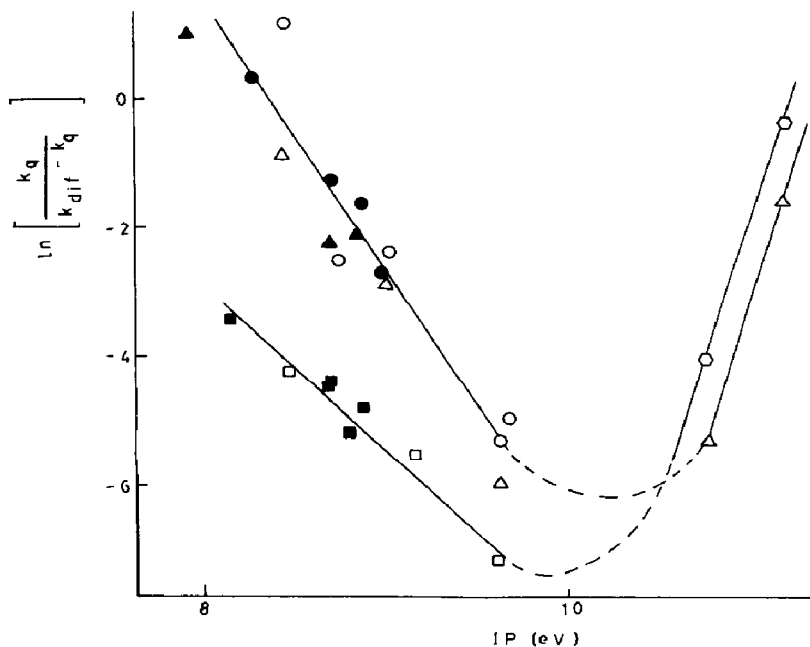


Fig. 2. The dependence of the rates of butanal and acetone fluorescence quenching by unsaturated compounds on their ionization potentials: ●, ○, butanal in *n*-hexane; ▲, △, butanal in acetonitrile; ■, □, acetone in *n*-hexane (from ref. 19); ○, acetone in acetonitrile (from ref. 19); ○, △, □, ○, olefins; ●, ▲, ■, 1,3-di-olefins.

selective and stereoselective manner, a process which is assumed to occur via the excited alkanal singlet [18].

Dalton *et al.* [6] have measured the rate of quenching of several alkanals by dicyanoethylene in acetonitrile and Shima *et al.* [7] have determined the rate of the reaction between excited propanal and several conjugated dienes in benzene. These authors have found that alkanals react considerably faster than alkanones and that the rate of the process is determined by the ionization potential of the di-olefin. In the present work we measured the rate of quenching of several aldehydes in *n*-hexane and acetonitrile by unsaturated compounds covering a wide range of ionization potentials in order to analyse the effects of the aldehyde, the quencher and the solvent. The results obtained are given in Table 2 and Fig. 2.

The results given in Table 2 do not show a clear relationship between reactivity and the alkanal structure. A similar result has been obtained by Dalton *et al.* employing triethylamine as quencher [6]. These results indicate that the rate of the quenching reaction is scarcely sensitive either to steric hindrance or to the electron affinities of the alkanals. The lack of a steric hindrance effect has been explained in terms of a preferential direction of approach of the quencher that avoids the bulky R group [6]. The electron affinity effect can be expected to be quite moderate. The change in  $k_Q$  associated with a given change in the alkanal reduction potential will be

similar to that obtained for a similar change in the ionization potential of the olefin. Thus the data of Fig. 2 indicate that even a change of 0.2 eV in the alkanal reduction potential would modify the rate of quenching by less than a factor of two. The reduction potentials of the alkanals are not available, but an insight into the magnitude of the change expected can be obtained by considering that the values for formaldehyde, acetaldehyde and acetone are  $-2.03$ ,  $-2.10$  and  $-2.30$  eV respectively.

The results given in Fig. 2 cover all the aliphatic olefins considered in the present work. These data show that similar values are obtained in *n*-hexane and acetonitrile, a result contrary to what could be expected for a reaction usually interpreted in terms of a charge transfer model. Yip *et al.* [19] have discussed similar results obtained in the quenching of triplet acetone by amines and have concluded that the absence of a dielectric constant effect can be compatible with the formation of a charge transfer complex that can react or revert back to the original reactants.

The data of Fig. 2 show, as in the alkanones [20], two branches that can be assigned to electron-rich (left-hand branch) and electron-deficient (right-hand branch) olefins. Also these data show that mono-olefins and diolefins have rate constants that can be included in the same correlation. In contrast, phenyl-substituted olefins (styrene,  $\alpha$ -methylstyrene and vinyl-toluene) have quenching rate constants almost ten times smaller than those expected from their ionization potentials.

The slope of the plot for the electron-rich olefins is nearly  $-3.8$  eV $^{-1}$ , a value significantly greater than that obtained when acetone is used (approximately  $-3.0$  eV $^{-1}$ ). In this case, as in some other carbonyl compounds [21], the more reactive compound shows the greater selectivity, a result contrary to the widely employed rule that relates selectivity to lack of reactivity. Nevertheless, it has to be considered that in the present case it can be expected that a larger amount of charge separation (favoured by a less negative reduction potential or by a closer approach) would increase both the reactivity and the dependence on the ionization potential.

The results obtained employing electron-deficient olefins, although limited, are quite different from those of the electron-rich olefins. The reactivity of acetone is greater than that of butanal, in the spite of a larger steric hindrance that could be expected for the former compound. The difference can be attributed to the lower ionization potential of the ketone.

The rate of quenching of an electron-deficient olefin must be correlated with the olefin reduction potential [21]. The change in rate observed between acrylonitrile and dicyanoethylene gives a slope of about 3 eV $^{-1}$ . This value is of the same order of magnitude as that obtained for electron-rich olefins. Similar results have been obtained in the quenching of triplet acetone by olefins [21].

### 3.4. Quenching by amines and hydrogen donors

The quenching of the fluorescence for several of the alkanals that can be photoreduced was investigated. The results obtained are given in Table 3.

TABLE 3

Specific rate constants for the singlet quenching by amines and hydrogen donors

Donor	Quencher <sup>a</sup>	$k_Q$ ( $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ )
<i>n</i> -Butanal	Triethylamine (7.8)	7.8 (8.9) <sup>b</sup>
Acetone	Triethylamine	2.7 <sup>c</sup>
<i>n</i> -Butanal	<i>n</i> -Butylamine (8.7)	4.9
Propanal	Hexanethiol	0.44
Acetone	Hexanethiol	0.47
<i>n</i> -Butanal	4- <i>tert</i> -Butylphenol	0.1
Propanal	Diethylhydroxylamine	6.1
Acetone	Diethylhydroxylamine	3.9

<sup>a</sup>The ionization potentials are given in parentheses.

<sup>b</sup>Data taken from ref. 6.

<sup>c</sup>Data taken from ref. 22.

Values obtained for acetone are included for comparison. Results obtained for 2-pentanone and amines indicate that photoreduction makes a significant contribution to the quenching process [23]. The same reaction can be assumed to occur with the other compounds employed since all of them have labile hydrogen atoms. In spite of the fact that 4-*tert*-butylphenol and hexanethiol have weaker bonds than the amines, the amines react considerably faster, a result that emphasizes the role played by charge transfer structures in the stabilization of the critical configuration. A similar conclusion has been reached regarding the reactions of alkoxy radicals (a good model for excited carbonyl compounds) with amines [24]. Triethylamine reacts with butanal singlets appreciably faster than *n*-butylamine, a difference that can be related to its lower ionization potential. The dependence of  $k_Q$  on the ionization potential of the amine seems to be considerably smaller than that obtained for the olefins (see Table 1). A similar difference is obtained when the singlets of the alkanones are considered [23] and could be explained in terms of a larger degree of reversibility after the production of a charge transfer complex [19]. *n*-Butanal reacts with the amines considerably faster than acetone, a result expected from the higher reduction potential of the alkanal [2]. In contrast, the results obtained employing hexanethiol indicate that propanal and acetone show similar reactivities in a process than can be considered as a simple hydrogen abstraction. A similar conclusion can be obtained from a comparison of  $(k_{II})_S$  values and implies that the fast auto-quenching observed in the alkanals is a consequence of the lability of the aldehydic hydrogen.



TABLE 4

Photoelimination quantum yield and  $(k_{Q\tau})_T$  values obtained at very low aldehyde concentrations

Aldehyde	$(\phi_{II}^{\circ})_T$	$(\phi_{II}^{\circ})_S$	$(k_{Q\tau})_T$	$\phi_T$
<i>n</i> -Butanal	0.047 <sup>a</sup> (0.11) <sup>b</sup>	0.036 (0.04) <sup>b</sup>	675 <sup>a</sup>	0.72 <sup>b</sup>
<i>n</i> -Pentanal	0.12	0.08	124	0.43 <sup>c</sup>

<sup>a</sup> Value obtained at  $[A] = 0.04$  M.

<sup>b</sup> Data taken from ref. 4.

<sup>c</sup> Derived from the relative fluorescence quantum yields of *n*-butanal and *n*-pentanal.

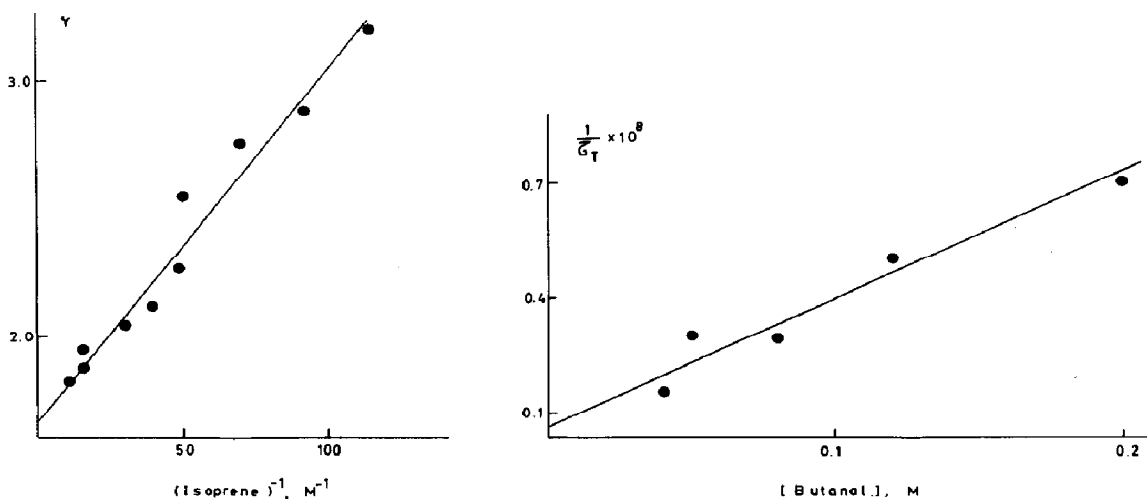


Fig. 3. A modified Stern-Volmer plot for triplet *n*-pentanal quenched by isoprene:

$$Y = \frac{\phi_{II}^{\circ}}{\phi_{II}^{\circ} - \phi_{II} \{1 + (k_{Q\tau})_S [Q]\}}$$

Fig. 4. The triplet lifetime as a function of *n*-butanal concentration in *n*-hexane.

### 3.5. Photoelimination from the singlet state

There are conflicting results regarding the relevance of singlet photoelimination. Lebourgeois *et al.* [2] have concluded that all reactions take place from the triplet state, while Coyle [1] and Forgeteg and Berces [4] consider that a significant fraction of the reaction originates from the singlet state. The evaluation of this fraction must take into account the competitive singlet quenching both by the alkanal itself and by the "selective" triplet quencher employed. A reaction scheme including quenching of both the singlet and triplet states leads to eqn. (12) for the photoelimination quantum yield  $\phi_{II}$ :

$$\frac{\phi_{II}^{\circ}}{\phi_{II}^{\circ} - \phi_{II}\{1 + (k_Q\tau)_S[Q]\}} = \frac{\phi_{II}^{\circ}}{(\phi_{II}^{\circ})_T} \{1 + (k_Q\tau)_T^{-1}[Q]^{-1}\} \quad (12)$$

Since  $(k_Q\tau)_S$  can be evaluated independently from fluorescence measurements, this equation allows the evaluation of  $(k_Q\tau)_T$  and  $(\phi_{II}^{\circ}/\phi_{II})_T$  by plotting the left-hand side against  $[Q]^{-1}$ . This type of plot for *n*-pentanal is shown in Fig. 3. The results obtained for *n*-butanal and *n*-pentanal are given in Table 4.

The results obtained for *n*-butanal are similar to those reported by Forgeteg and Berces [4]. *n*-Pentanal shows, as in the alkanones [8], a larger  $(\phi_{II})_S$  than the compound bearing primary  $\gamma$  hydrogens. The results of Table 4 allow an estimation of the fraction  $\beta$  of biradicals that gives type II photo-products. The values obtained for  $\beta_S$  and  $\beta_T$  are 0.14 and 0.15 for *n*-butanal, and 0.14 and 0.27 for *n*-pentanal. The values of  $\beta_S$  are then similar to those reported for 2-pentanone and 2-hexanone [8]. In contrast, the values of  $\beta_T$ , although showing a similar increase with the increase in the alkyl chain, are considerably smaller than those reported for the alkanones [8]. The fact that  $\beta_S$  and  $\beta_T$  are equal in *n*-butanal is compatible with the large rate of rotation expected in these biradicals.

### 3.6. Triplet reactions

The plot shown in Fig. 3 allows the evaluation of  $(k_Q\tau)_T$ . The values obtained for *n*-pentanal were independent of the aldehyde concentration, while for *n*-butanal a decrease in  $(k_Q\tau)_T$  was observed when the aldehyde concentration was increased. A plot of  $\tau_T^{-1}$  against the concentration of butanal is shown in Fig. 4, for  $k_Q$  taken as  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . This plot allows the evaluation of the rate constant of the reaction



giving  $k_{13} = 3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . This value is similar to that reported by Forgeteg and Berces [4] ( $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) from the change in the photo-products quantum yield, and by Lebourgeois *et al.* [2] ( $7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) from the change in the alkanal consumption quantum yield. These values are almost an order of magnitude smaller than those found for the singlet autoquenching, a result that can be explained in terms of the smaller exothermicity of the triplet reaction. It is interesting to note that the selectivity in the autoquenching is smaller than that of the intramolecular hydrogen abstraction, a result compatible with the lability of the aldehydic hydrogen.

The effect of the aldehyde concentration on the photochemistry arising in the triplet state could alternatively be explained by a reaction between the triplet biradical produced in the intramolecular hydrogen abstraction and the alkanal. Nevertheless the fact that the results obtained employing *n*-pentanal are not dependent on the aldehyde concentration rules out this

possibility. A similar conclusion has also been reached by Forgeteg and Berces [4] from results obtained employing deuterated aldehydes\*.

The data shown in Fig. 4 allow the evaluation of  $\tau_T$  under conditions where the autoquenching can be disregarded. The values obtained were  $2.5 \times 10^{-7}$  s for butanal and  $1.24 \times 10^{-8}$  s for pentanal. The first value differs by a factor of two from that estimated by Forgeteg and Berces [4], a difference that can be caused by the error involved in the extrapolation to zero concentration. The value obtained for *n*-pentanal is a factor of two larger than that reported by Coyle [1] in benzene. The difference in this case is probably due to neglecting singlet quenching by the diene. The values of  $\tau_T$  allow an estimation of  $k_{II}$  from the triplet. The values obtained are  $k_{II} = 3 \times 10^6$  s<sup>-1</sup> for butanal and  $k_{II} = 8 \times 10^7$  s<sup>-1</sup> for pentanal. The value for butanal is affected by a rather large error (a factor of two), *i.e.* the experimental error and the unknown contribution of type I photofragmentation. These values are similar to those obtained for 2-pentanone ( $3.9 \times 10^6$  s) and 2-hexanone ( $1.6 \times 10^8$  s<sup>-1</sup>) [25].

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\*These results are not conclusive owing to the lower rate expected for the abstraction of a deuterium atom. Similarly, the reaction between a biradical and an alkanol molecule followed by cage disproportionation would also produce molecules of an alcohol with two deuterium atoms in the alkyl chain.

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