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PHOTOCHEMISTRY IN SOLUTION—XX

TRIPLET REACTIVITY OF ALIPHATIC ALDEHYDES

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Abstract—The triplet self-quenching process of three aliphatic aldehydes has been investigated by inhibition with dienes (taking into account the singlet interaction with the dienes) and by laser flash photolysis. The results obtained for intersystem crossing, the self-quenching process and product formation have been rationalized. The main reactivity observed for the three aldehydes is the self-quenching process which occurs from both the singlet and triplet state. The laser flash photolysis experiments carried out with butanal show two absorptions of a transient at 320 and 355 nm; no evidence for two different species could be put forward. The similar decay of the two absorption maximas of the transient, as the concentration of aldehyde is increased, would be indicative of only one single absorbing species which could be either the triplet state of the aldehyde or a radical-pair formed by the self-quenching process or the 1,4-biradical resulting from γ-H abstraction. The fact that both the quenching experiments (by dienes or by 1-methylnaphthalene) and the laser flash measurements lead to about the same lifetime also indicates only one species.

The products formed from the triplet self-quenching process have also been obtained by a different method: excitation of benzophenone at 365 nm in the presence of butanal. The quantum yields for product formation is about the same as those obtained for the triplet by direct irradiation of butanal, except that of octane-4,5-dione which is increased if the photoreaction is carried out at 365 nm in the presence of benzophenone.

The photochemical behaviour of aliphatic and aromatic aldehydes has been investigated by several groups and fragmentary results were reported in different cases. Thus, it was observed[1] that aliphatic aldehydes undergo photodecarbonylation by direct irradiation or by sensitization with aromatic ketones. The sensitized reaction was re-investigated[2] and α-cleavage was proposed as an explanation for the decarbonylation. This suggestion is in good agreement with the observation[3] that α-cleavage of aliphatic aldehydes originates from both the singlet and triplet excited states. A puzzling result was later reported[4] for the decarbonylation of α-arylaldehydes: The chemically induced dynamic nuclear polarization (CIDNP) favours a triplet state although no triplet quenching nor triplet sensitization could be characterized in that case. It was noted that the CIDNP signals could arise "from a smaller triplet-born radical pair component which is undetected in scavenging and quenching attempts". Simultaneously, the Norrish type II reaction was characterized for a series of aliphatic aldehydes.[5] Only recently, was it found that aldehydes undergo a self-quenching process from the singlet state[6,7] and from the triplet state.[7,8]

The triplet self-quenching process was characterized independently by spin nuclear polarization and by chemically induced dynamic nuclear polarization (CIDNP) in the case of ethanal,[9] propanal[10] and benzaldehyde.[11] In the latter case, the Φ-ĊHOH radical, formed by abstraction of the aldehydic hydrogen of a ground state aldehyde molecule by a triplet excited benzaldehyde molecule, was observed to undergo the following reaction step (where the asterisk indicates the spin polarization):

$$(\Phi\text{-}\dot{C}HOH)^* + \Phi\text{-}CHO \longrightarrow (\Phi\text{-}CHO)^* + \Phi\text{-}\dot{C}HOH$$

Because of the singlet self-quenching process,[12] access to the triplet state would decrease and result in a lower triplet reaction at higher aldehyde concentrations. The intersystem crossing process has also been found to decrease with the length of the chain of the aliphatic aldehyde from 0.64 for propanal to 0.18 for heptanal.[12] Our own measurements, using the method of Lamola and Hammond,[13] lead to the values given in Table 1.

Aldehydes react from their singlet state with dienes to form oxetanes[14] with a rate constant of about one fourth that of diffusion control. Thus, this competitive process may not be negligible when the concentration of the diene becomes high.

The triplet lifetime of several aldehydes has been measured (35 ns for butanal; 6.2 ns for hexanal)[5] but the data are specific for a given concentration in aldehyde because of the triplet self-quenching process which was not taken into account for the measurements. The triplet lifetime of butanal was measured independently[15] and the $k_q\tau_T$ value (4000 l.mole^{-1}) obtained in iso-octane solution is indicative of a lifetime of *ca.* 300 ns. Lifetimes of 22 ns and 14 ns were also determined[16] for 2-ethylbutanal and pivaldehyde respectively. Similar values are reported for aliphatic methylketones; for instance, 2-pentanone has a triplet lifetime of 78 ns[17] or 16 ns[18] both in benzene solution while a 250 ns lifetime has been measured[18] in hexane solution. Much shorter values were determined for ketones which undergo Norrish type II reaction with secondary γ-hydrogen atoms (5 to 10 ns in both solvents).[18] In this paper we examine the intersystem crossing of aldehydes **1**–**8**, the phosphorescence of several of them and the photochemistry of **2**, **3** and **6** with the aim of understanding the processes which control their photochemical behaviour. The combination of laser flash photolysis with traditional quantum yield and quenching experiments help characterize the fugacious intermediates. A recent study on 1,5-diaryl-1,5-diketones[19] indicates that arylketones can have rather

Table 1. Intersystem crossing quantum yield and rate constant of aldehydes 1 to 8 (0.2 molar in pentane solution).

aldehyde	1	2	3	4	5	6	7	8
τ_s (ns)[#]	1.8	1.7	1.0	1.1	1.1	1.3	1.8	1.6
ϕ_{isc}[¶]	0.5_5 (0.64)[a]	0.4_5 (0.47)[a]	0.3	0.3[§]	0.3[§] (0.18)[a]	0.6 (0.5)[b]	0.6[×] (0.5)[b]	0.5
$k_{isc} \times 10^{-8}(s^{-1})$	2.5	2.7	3.0	2.6	2.6	4.5	3.0	3.0

Values are given with ± 15 % error on ϕ_{isc} and 20 % on k_{isc}.

[#] The singlet lifetime of the aldehydes are measured for concentrations 0.2 in aldehyde and 0.11 in *cis*-piperylene.

[¶] Data are corrected for aldehydes 1, 2, 3 and 6 ; uncorrected for 8.

[§] Assumed for the correction to behave like 3.

[×] Assumed to behave like 6 (since α-cleavage is the main deactivation step).

(a) Taken from reference 12.

(b) Taken from reference 16.

long triplet lifetimes (*ca.* 50 ns) but that the triplet state decays to give 1,4-diradicals which have lifetimes of about the same order as the triplet itself. Similar behaviour had been pointed out for the case of polyphenylvinylketone, where the signal assigned for the biradical is rather long-lived.[20]

$CH_3(CH_2)_nCHO$	$(R)_2CHCHO$	$(CH_3)_2CH(CH_2)_2CHO$
1 n = 1	6 R = CH_3	8
2 n = 2	7 R = C_2H_5	
3 n = 3		
4 n = 4		
5 n = 5		

RESULTS

Intersystem crossing. Intersystem crossing efficiencies ϕ_{isc} were measured at a given concentration (0.2 M) of the aldehyde using the sensitized $Z \rightarrow E$ isomerization of piperylene.[13] Limited conversion (3 to 6%) was used in order to minimize the reverse isomerization. Exact values can only be obtained by knowing the amount of triplet aldehyde quenched by the diene at the concentration (0.11 M) used for the intersystem crossing quantum yield measurements. The amount of unquenched triplet has been determined for aldehydes 1, 2, 3 and 6 and found to be 1%, 1%, 3% and 10% respectively. The intersystem crossing quantum yield obtained had to be corrected by this factor. The ϕ_{isc} values were calculated by comparison with 4,4-dimethylcyclohexanone for which ϕ_{isc} has been found to be 0.93.[21] For the other aldehydes studied, the amount of triplet quenching has not been measured precisely. 2-Ethylbutanal 7 is believed to behave similarly to 6 since α-cleavage appears to be the main deactivation pathway for the α-alkylated aliphatic aldehyde 6. On the other hand, haxanal 4 and heptanal 5 were not very different from pentanal 3. Consequently, only the value obtained for 8 would be uncorrected. The values obtained for aldehydes 1 to 8 are given in Table 1.

Phosphorescence. The phosphorescence spectra of aldehydes 1 and 4 to 8 at 77K in a methylcyclohexane glass are similar to those of aliphatic ketones. The maximum of the emission occurs around 450 nm and the vibrational structure observed in several cases puts the 0–0 band at about 375 nm corresponding to *ca.* 76 kcal/mole.

Product formation. Since the products result from the interaction between two molecules of aldehyde, the quantum yield for their formation will fluctuate with the concentration of aldehyde. Direct irradiation of the aldehyde RCHO leads to a mixture of at least six compounds: the corresponding primary alcohol RCH_2OH, the α-ketol R–CO–CHOH–R, the ketone R–CO–R and its reduced form R–CHOH–R, the α-diketone R–CO–CO–R and the α-diol R–CHOH–CHOH–R. The latter decomposes on the VPC apparatus to give the ketone R–CO–CH_2–R by way of a pinacol rearrangement. When γ-H atoms are available, as for 2 and 3, the Norrish type II reaction forms photoelimination products as well as a cyclobutanol; only the latter has been isolated. In all the cases studied, the α-ketol predominates in the direct irradiation experiments. In the presence of a triplet quencher, the only products characterized are the cyclobutanol, the primary alcohol and the α-ketol. The formation of these three compounds decreases by a factor which varies from one product to another. In the case of 2, 3 and 6, the quantum yields for product formation have been determined for pentane solutions 0.2 molar in aldehyde under 313 nm light irradiation. The results given in Table 2 are obtained for about 15% conversion; they do not take into account the β-cleavage reaction which occurs for compounds 2 and 3. Values measured by other authors are included in the Table. The quantum yields resulting from the singlet state have been determined by triplet quenching experiments, using 2,5-dimethyl-2,4-hexadiene or 1-methylnaphthalene as quencher.

Laser flash photolysis. Laser flash photolysis experiments have been carried out with a Neodym glass laser with frequency quadrupling (265 nm, 30 ns, 20 mJ). The absorption spectra of the transient has been obtained

Table 2. Quantum yields for product formation by direct irradiation of aldehydes 2, 3, and 6 (0.2 molar in pentane solution) in the presence or in the absence of a triplet quencher, and in the benzophenone induced reaction.

Aldehyde RCHO / Product Formed	2 (R=Pr)				3 (R=Bu)		6 (R=iPr)	
	Direct irradiation (313nm)			with benzophenone (366nm)				
	S + T	$S^{\#}$	$T^{\#}$		S+T	$S^{\P}$	S+T	$S^{\P}$
R-CH_2OH	0.08_5	0.03	0.05_5	0.08	0.06_2	0.01	0.09_2	0.02_8
R-CHOH-CO-R	0.15	0.05_8	0.09_2	0.07	0.09_3	0.05_6	0.13	0.11_7
Cyclobutanol	0.03_4	0.02_2	0.01_2	—	0.02_4	0.01_7	—	—
	$(0.03_4)^{×}$	$(0.00_7)^{×}$	$(0.02_7)^{×}$					
R-CHOH-R	0.11	—	0.11	0.03	0.08	--	0.07	—
R-CO-R	0.08	—	0.08	0.08	0.07_5	--	0.11	—
R-CO-CO-R	0.05_8	—	0.05_8·	0.06	0.04_3	--	0.05_7	···
R-CH_2-CO-R	0.00_7	--	0.00_7	—	$<10^{-3}$	--	$<10^{-3}$	--
β-cleavage	$(0.14)^{×}$	$(0.03_5)^{×}$	$(0.10_5)^{×}$		$(0.10)^{§}$			

\# quenching by 2,5-dimethyl-2,4-hexadiene or by 1-methylnaphtalene ;

¶ quenching by 2,5-dimethyl-2,4-hexadiene ;

× taken from reference (25) ;

§ deduced from the ratio 0.25 given by Coyle[5] between cyclobutanol formation and β-cleavage.

from butanal 2 in pentane by detection at different wavelengths and at different times after the peak of the excitation pulse. The spectra, shown in Fig. 1, are characterized by two absorption maxima, one at 320 nm and the other at 355 nm. This absorption is slightly shifted (by about 15 nm) when compared to the triplet-triplet absorption of acetone[22] which shows only one maximum. On the other hand, this spectrum can be compared to that of an aromatic ketone as described by Faure *et al.*[20] and by Scaiano *et al.*,[19] but with a shift of about 80 nm toward shorter wavelengths. According to Scaiano, the double maxima could be attributed to the triplet excited state and to a triplet biradical as found for 1,5-diphenylpenta-1,5-dione, for which the two maxima are at 405 and 450 nm. In the case of butanal, the optical density of the transient species decreases with the same rate at both wavelengths; 380 ns after the laser pulse, there still remains a residual transient absorption which can be attributed to radicals.

The decrease of the excited species with initial concentration C_0 can be expressed by

$$C = C_0 \exp(-t/\tau) \qquad \text{(I)}$$

where τ represents the lifetime of this excited species. Since the vertical deviation y recorded on the oscilloscope is proportional to C ($C = ky$) the expression becomes

$$\ln y = \ln y_0 - \frac{t}{\tau} \qquad \text{(II)}$$

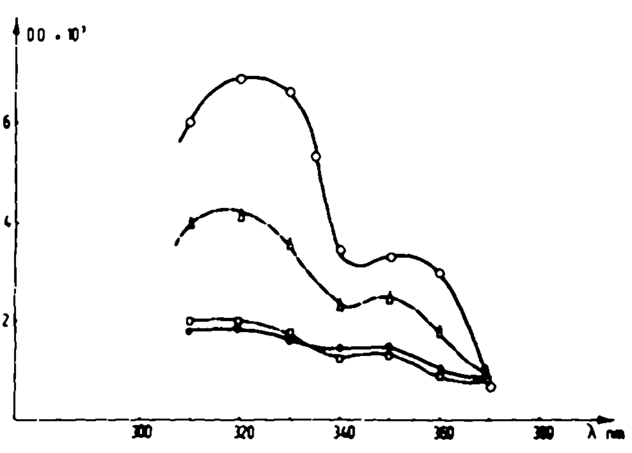


Fig. 1. Laser flash photolysis of butanal 2. Transient absorption: ○, immediately after the laser impulsion; △, 180 ns after the laser impulsion; □, 380 ns after the laser impulsion; ●, 900 ns after the laser impulsion.

Thus, the curve $\ln y = f(t)$ will be a straight line with a $-1/\tau$ slope.

The concentration of the aldehyde must be chosen so as to meet two contradictory requirements: small enough to minimize the self-quenching process of the triplet species but high enough to detect the absorption of the species. For this reason, only butanal could be analyzed at different concentrations, while the only one for which a correct analysis could be performed was 0.55 M in the case of pentanal. No transient could be detected for isobutanal, probably because of its very short lifetime (*vide infra*).

The lifetime of the excited species has been measured for various concentrations in butanal and the resulting values are shown in Table 3. The results indicate a clear increase as the concentration of the aldehyde decreases; a typical indication of a self-quenching process.

Quenching studies. The quenching experiments were carried out by using 2,5 - dimethyl - 2,4 - hexadiene as the triplet quencher and taking the rate constant for quenching as $(1.5 \pm 0.2) \times 10^{10}\,M^{-1}\,s^{-1}$. This value is deduced from the slope of the usual Stern-Volmer plot and from the lifetime of the species characterized by laser flash-photolysis in pentane solution. Since dienes efficiently inhibit the fluorescence of aldehydes,[6,14] the usual Stern–Volmer relation has to be changed to the more general expression (III):[23]

$$\frac{\phi^\circ}{\phi} = [1 + k_q{}^s\tau_s^\circ[Q]][1 + k_q{}'\tau_t^\circ[Q]]\,\frac{1 + (\phi_t^\circ/\phi_s^\circ)}{1 + (\phi_t^\circ/\phi_s^\circ) + k_q{}'\tau_t^\circ[Q]} \tag{III}$$

where ϕ° and ϕ are the quantum yields for product formation in the absence and in the presence of the inhibitor Q; ϕ_t° and $k_q{}'$ are the quantum yield from the triplet state and the rate constant of triplet quenching reaction by the diene respectively; ϕ_s° and $k_q{}^s$ refer to the singlet state; τ_s° and τ_t° are the singlet and triplet state lifetimes of the aldehyde at the given concentration and in the absence of the diene. When the concentration of the quencher is limited to low values, the curve is a straight line, the initial slope of which (IV) is deduced from the previous expression and can be described in the following fashion.

$$\text{initial slope} = k_q{}^s\tau_s^\circ\,\frac{\phi_t^\circ}{\phi_t^\circ + \phi_s^\circ}\,k_q{}'\tau_t^\circ \tag{IV}$$

In the case of butanal **2**, pentanal **3** and isobutanal **6**, the experimental value for the slope is $820 \pm 45\,M^{-1}$, $340 \pm 25\,M^{-1}$ and $47 \pm 5\,M^{-1}$ respectively. At the given concentration in aldehyde (0.22 M), the singlet lifetime was found to be 2.9 ns, 1.5 ns and 1.7 ns for **2**, **3** and **6**; this leads to the corresponding values of 12, 6 and 7 M^{-1} for $k_q{}^s\tau_s^\circ$ respectively. The measurements based on the formation of the primary alcohol indicate that the triplet reaction represents 65%, 85% and 70% of the total reaction from aldehyde **2**, **3** and **6** respectively. Application of expressions (III) and (IV) to the measured values leads to 1,250, 390 and 57 M^{-1} respectively for the $k_q{}'\tau_t^\circ$ value of the triplet quenching of the formation of the primary alcohol from **2**, **3** and **6** for a concentration 0.22 in aldehyde.

The exact value of the rate constant for quenching the triplet excited state by the diene has been averaged from three quenching experiments of product formation at different concentrations in butanal (0.11, 0.22 and 0.33 M). The result obtained with a concentration 0.22 in **2** has been discussed above: $1{,}250\,M^{-1}$. At a concentration 0.11 M, butanal has a singlet lifetime of 3.3 ns and the initial slope measured is $1200\,M^{-1}$; the lifetime of the species, characterized by laser flash photolysis as the triplet excited state, is 115 ns for this concentration. Application of expression (IV) leads to a true $k_q{}'\tau_t^\circ$ of $1{,}800\,M^{-1}$ and, consequently, to a quenching rate constant of $1.5 \times 10^{10}\,M^{-1}\,s^{-1}$. For a concentration 0.33 M in butanal ($\tau_s^\circ = 2.3$ ns; $\tau_t^\circ = 66$ ns) the experimental slope is $550\,M^{-1}$; correction leads to a true value of $840\,M^{-1}$ and thus, to a triplet quenching rate constant of $1.3 \times 10^{10}\,M^{-1}\,s^{-1}$. The average of the three measurements is then $(1.5 \pm 0.2) \times 10^{10}\,M^{-1}\,s^{-1}$. This value is close to that measured by Wagner and Kochevar[24] for valerophenone in pentane solution: $1.32 \times 10^{10}\,M^{-1}\,s^{-1}$.

Quenching experiments of the product formation from

Table 3. Triplet self-quenching results and lifetimes at infinite dilution.

ALDEHYDE	concentration (M)	Laser flash analysis		quenching by dienes					
		τ (ns)	$\frac{1}{\tau} \times 10^{-6}\,s^{-1}$	$k\tau$ uncorrected	$k\tau$ corrected	τ (ns)	$\frac{1}{\tau} \times 10^{-6}\,s^{-1}$	$k_{sq} \times 10^{-7}$ ($M^{-1}s^{-1}$)	τ^∞ (ns)
BUTANAL	0.055	170	5.9						
	0.11	115	8.7	1200	1800	120	8.3		
	0.17	94	10.6						
	0.22	86	11.6	820	1250	83	12.0	3.9	250
	0.27	80	12.5						
	0.33	66	15.2	550	840	56	17.8	(3.1)*	(210)*
	0.44			.480	720	48	20.8		
PENTANAL	0.055	50	20						
	0.11			500	580	39	25.5		
	0.20			350	400	27	37		
	0.22			340	390	23	43.5	16.7	170
	0.31			230	260	17	59		
	0.39			180 350†	200	14 35†	71.5		
ISOBUTANAL	0.18			48	60	4	250		
	0.22			47	57	3.8	260	35	5.5
	0.26			45	54	3.6	280		
	0.36			42	50	3.3	300		
	0.55			35	40	2.7	370		
	0.66			32	36	2.4	420		

* from the laser flash photolysis experiments

† taken from reference 31

butanal (0.22 M), using 1-methylnaphthalene as the quencher have to be corrected as the quencher also absorbs the 313 nm light ($\epsilon = 250\,M\,cm^{-1}$). The slope of the Stern–Volmer plot (corrected from the light absorption by 1-methylnaphthalene is $1{,}040 \pm 150\,M^{-1}$. The quenching rate constant deduced from this experiment ($1.1 \times 10^{10}\,M^{-1}\,s^{-1}$) is somewhat lower than that obtained with the diene as quencher.

Triplet self-quenching process. The results from CIDNP measurements[9-11] clearly indicate that aldehydes undergo a self-quenching reaction from the triplet excited state; this was corroborated for butanal by Lemaire *et al.*[8] Similarly, the investigation of Cerfontain *et al.*[7] with cycloalkane carbaldehydes pointed out that the products of dimeric structure have a triplet origin. The variation of the lifetime of the species characterized by laser flash photolysis (Table 2, Fig. 1) is consistent with a self-quenching process which obeys the following expression:

$$\frac{1}{\tau^0} = \frac{1}{\tau^\infty} + k_{sq}[A] \qquad (V)$$

where τ^0 refers to the lifetime of the species for a concentration [A] in aldehyde, k_{sq} to the self-quenching process rate constant and τ^∞ to the lifetime of the species at infinite dilution. In the case of butanal, extrapolation of the curve to the intercept with the Y-axis gives a value of $(1/\tau^\infty) = 4.8 \times 10^6\,s^{-1}$ and consequently a lifetime at infinite dilution of $\tau^\infty = 210$ ns. The rate constant for the self-quenching process, k_{sq}, given by the slope of the curve is $3.1 \times 10^7\,l\,mole^{-1}\,s^{-1}$.

The triplet of pentanal and isobutanal is too short lived to be measured with the laser flash photolysis equipment used.

Dienes quench both the singlet state[6,14,26] and the triplet state of aldehydes. The rate constant for quenching the singlet state by 2,5 - dimethyl - 2,4 - hexadiene is known[14] to be of the order of $3.5 \times 10^9\,M^{-1}\,s^{-1}$ from fluorescence inhibition measurements. It has been shown, above, that the rate constant for quenching the triplet state of butanal is about $1.5 \times 10^{10}\,M^{-1}\,s^{-1}$. The usual Stern–Volmer plot and application of relations (III) and (IV) yield the triplet lifetime of aldehydes **2**, **3** and **6**; this, repeated for various concentrations in aldehydes, leads to the series of values given in Table 3. By plotting the inverse of the lifetime vs the concentration in aldehyde, linear relations are obtained (Figs. 2 and 3). The rate constant for the triplet self-quenching process of aldehydes **2**, **3** and **6**, deduced from relation (V) is found in Table 3.

The lifetime at infinite dilution τ^∞ is deduced from the intercept of the curve with the y-axis; the following values are obtained by this method: 210 ns for butanal from the laser flash photolysis experiments; 250 ns for

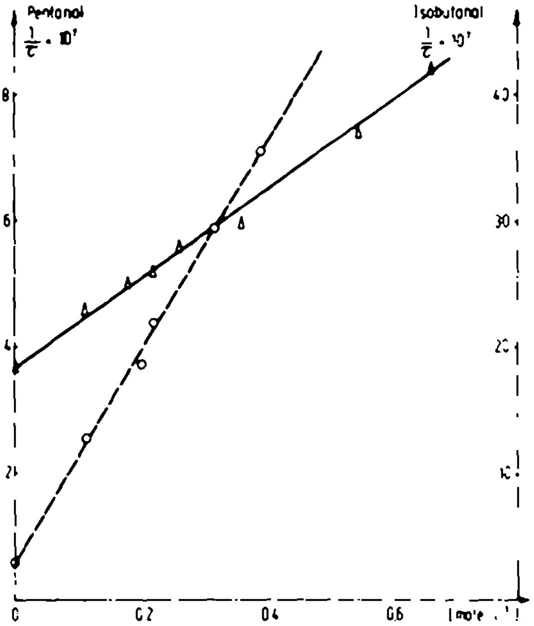


Fig. 3. Self-quenching process of: ○, pentanal **3**; △, isobutanal **6**. Lifetime values are from quenching by diene experiments.

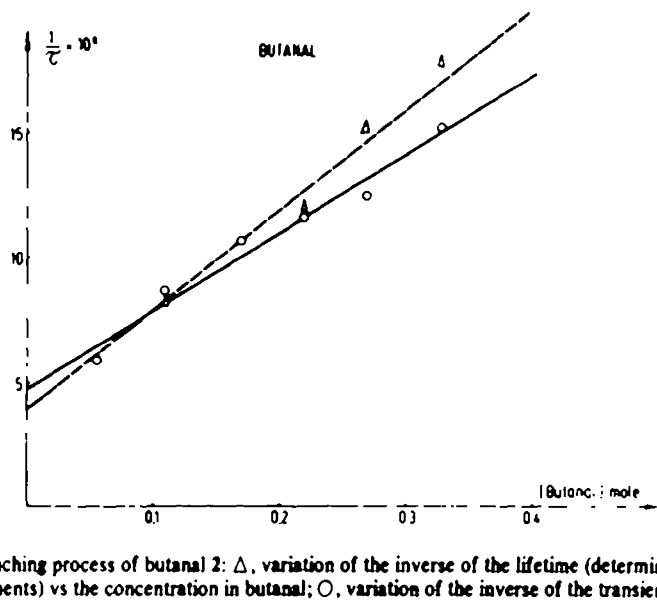


Fig. 2. Self-quenching process of butanal **2**: △, variation of the inverse of the lifetime (determined from quenching by diene experiments) vs the concentration in butanal; ○, variation of the inverse of the transient (characterized by laser flash photolysis) vs the concentration in butanal.

the same compound but using the values measured by the quenching in the diene experiments. In the case of pentanal 3 and isobutanal 6, the τ^{∞} values obtained are 170 ns and 5.5 ns respectively.

DISCUSSION

The lifetime of the excited species, characterized by laser flash photolysis for butanal and by quenching by the dienes for 2 and 3, is rather long for a carbonyl triplet excited state. 4,4-Dimethylcyclohexanone has a triplet lifetime of 84 ns,[21] but cannot give the Norrish type II reaction; in the same series, the triplet biradical formed by α-cleavage has a lifetime of about 1 μs. As noted above, the triplet lifetime of aliphatic ketones varies with the solvent[17,18] and can be rather long when the Norrish type II reaction involves abstraction of primary γ-H atoms. Also, a lifetime of 52 ns has been attributed to the triplet state of 1,5 - diphenyl - 1,5 - pentanedione in benzene solution;[19] but in the case of polyphenylvinylketone, Faure *et al.*[20] have attributed the long-lived transient, characterized by laser flash photolysis, to a triplet biradical resulting from the Norrish type II reaction. In that case, the absorption of the transient also shows two maximas as found here for butanal; but then the conjugation with the aromatic ring shifts the transient absorption to longer wavelength. Two maximas are observed with 1,5 - diphenyl - 1,5 - pentanedione but they decrease with a different lifetime.[19] It has been concluded that one of the maxima is the result of triplet triplet absorption while the other is due to the absorption of the triplet 1,4-biradical formed by γ-H abstraction. It would be very tempting, by analogy, to attribute the two absorption maxima observed for butanal to two specific species; one being the excited triplet state and the other the triplet radical-pair formed by abstraction of the aldehydic hydrogen of a ground state aldehyde by the excited triplet CO group of another aldehyde molecule:

$$(\mathrm{R{-}CHO^{*}})^{3} + \mathrm{RCHO} \longrightarrow \overline{\mathrm{R{-}\dot{C}HOH} + \mathrm{R{-}\dot{C}=O}}^{\,3}$$

The shift of the absorption toward short wavelengths, as compared to aromatic ketones, is plausible since there is no extended conjugation. The fact that the two maxima at 320 and 355 nm both decrease with the same rate when the concentration in butanal is varied favours a single absorbing species.

The quenching of the aldehyde triplet excited state by dienes is expected to be diffusion controlled. Since the quenching process is measured by the decrease of the quantum yield of butanol formation, any variation in the number of excited triplet species will result in the same variation of the number of triplet radical-pairs. An identical result would be reached if the diene quenched the triplet radical-pair instead of the triplet excited aldehyde. Such a situation would occur if the latter species was rather short lived and, consequently, hardly quenched by dienes. Although simple biradicals react very inefficiently with dienes[27] α-keto radicals are more reactive, as a result of an increased electron-attracting property.[28] On the other hand, the acyl radicals react with moderate efficiency with electron-deficient double bonds, such as α,β-unsaturated ketones[29] or α,β-unsaturated esters[30] leading to γ-diketones and γ-keto-esters respectively. In the presence of dienes, irradiation of aliphatic aldehydes yields oxetanes and not products resulting from the addition of acyl radicals to the conjugated unsaturated system (see for instance ref. 14 and refs cited therein). Thus, the chances that dienes chemically quench the acyl radical of the triplet radical pair $\overline{\mathrm{R{-}\dot{C}HOH} + \mathrm{R{-}\dot{C}=O}}^{\,3}$ are rather small. Nevertheless, if dienes were only quenching the CO triplet state and not the triplet radical-pair, one would expect the intensity of the latter to decrease but not its lifetime. Similarly if a self-quenching process took place at the level of the carbonyl excited triplet state, its lifetime would decrease with an increase in aldehyde concentration, but there would be no effect on the lifetime of the triplet radical-pair (though its intensity should increase with the concentration in aldehyde), unless there is a reaction step which involves the interaction between the triplet radical-pair and a ground state aldehyde molecule. Such a process has been observed by CIDNP (*vide supra*) between an aldehyde molecule and the $\mathrm{R{-}\dot{C}HOH}$ radical. Whether the radical is free in solution or still coupled in the triplet radical-pair can only be speculative.

Surprisingly, the aldehydes 2 and 3, which can undergo the Norrish type II process show a "triplet" lifetime at infinite dilution that is rather long. Similar results have been reported by Encina and Scaiano[31] who found that the triplet lifetime of pentanal 3 is of the order of 35 ns (out no specific concentration of the aldehyde was indicated) and who observed a second transient with a lifetime of 2 μs that they attributed to the triplet biradical resulting from γ-H abstraction.

In the case of isobutanal 6, the lifetime obtained by quenching the formation of isobutanol by dienes has been extrapolated to 5.5 ns at infinite dilution. Such a small lifetime could be attributed to an efficient α-cleavage reaction forming the isopropyl radical.

Irradiation of isobutanal in the presence of ethyl 2-butenoate forms a mixture of ethyl 3,4 - dimethylpentanoate and ethyl 3,4 - dimethyl - 2 - isopropylpentanoate, besides the α-ketol of mostly singlet origin.[30] The necessary isopropyl radical can be the result of two different reactions; either it involves α-cleavage directly from the triplet state, or a triplet self-quenching process which degenerates by decarbonylation of the $\mathrm{Me_2CH{-}\dot{C}=O}$ acyl radical. In the latter case, one would expect formation of 2,4 - dimethyl - 3 - pentanol by coupling of the isopropyl radical with the $\rangle\!{-}\dot{\mathrm{C}}\mathrm{HOH}$ radical. The results obtained (Table 2) disfavour such a mechanism and, consequently, would be more in favour of the direct α-cleavage from the CO excited triplet state. If so, comparison of the lifetime of butanal with that of isobutanal would give a rough value (*ca.* $2 \times 10^{8}\ \mathrm{s^{-1}}$) of the rate constant for α-cleavage of isobutanal. This is not very different from what has been found ($1.7 \times 10^{8}\ \mathrm{s^{-1}}$) for the α-cleavage rate constant of 2,4,4 - trimethylcyclohexanone.[21] However, if the triplet lifetime of the aldehydes was of the order of the ns and that of the triplet radical pair $\overline{\mathrm{R{-}\dot{C}HOH} + \mathrm{R{-}\dot{C}=O}}^{\,3}$ measured on the 100 ns scale, one would still have expected to observe the absorption (with either one or two maximas) build up from isobutanal of the long-lived transient in the laser flash photolysis. Since no absorption could be detected 30 ns after excitation of isobutanal by the laser, the transient detected in the case of the other two aldehydes may be attributed to a long-lived triplet excited state of thecarbonyl group rather than to the radical-pair.

This conclusion is in good agreement with recent results observed[32] by laser flash photolysis for aliphatic ketones which show a rather long-lived triplet transient in acetonitrile solution: 111 ns for 2-pentanone and 272 ns for 2-butanone. A lifetime of *ca.* 4 μs has been attributed to the 1,4-biradical given by the Norrish type II reaction of 5 - methyl - 2 - hexanone.

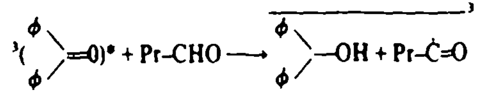
Chain reaction from the triplet radical pair

The assumption that the formation of pinacol from aromatic ketones was quenched by aldehydes by triplet energy transfer has been promptly ruled out and corrected into a chemical quenching process. It is known also that mixtures of substituted benzophenones and benzhydrols give a chain reaction,[33] the mechanism of which has been rationalized in terms of a hydrogen atom exchange between a ketyl radical and a ground state benzophenone:[34]

$$(C_6H_5)_2\dot{C}{-}OH + (C_6D_5)_2C{=}O \longrightarrow (C_6H_5)_2C{=}O + (C_6D_5)_2\dot{C}{-}OH$$

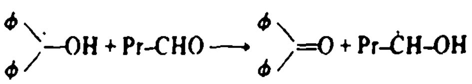
Recent CIDNP measurements[9-11] clearly indicate that a similar chain radical process occurs between a ground state aldehyde molecule and a R–$\dot{C}$HOH radical formed in the self-quenching photoprocess of aldehydes R-CHO.

It was of interest to look into the chemical evolution of such a radical chain by combining the two different reactions. Thus, benzophenone (9×10^{-2} M) has been irradiated in the presence of a large excess (0.5 M) of butanal in such a way that only the aromatic ketone absorbs the light (excitation at 366 nm). The first step of the photoreduction of benzophenone, under these conditions, will be the abstraction of the hydrogen atom from the lowest energy C-H bond of the counterpart; here, this will be the aldehydic C-H bond, the energy of which is *ca.* 86 kcal/mole:[35]



(A)

The two radicals of the formed triplet radical-pair will not couple together but first diffuse apart from each other. Then, the ketyl radical will undergo the usual chain reaction with the carbonyl species present in the solution that is to say, here, with butanal:



(B)

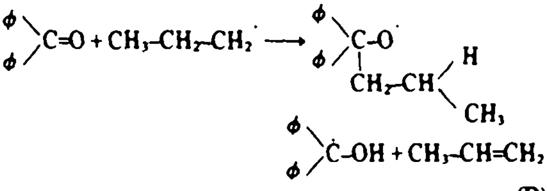
Consequently, the radicals found in the solution will be, very rapidly, the same as the ones obtained during the self-quenching photoprocess of butanal. The main difference will lie with the relative ratio of the various products formed since the α-ketol, octan - 4 - ol - 5 - one, and cyclobutanol resulting from direct irradiation have a singlet and a triplet origin while the other dimeric products arise from only the triplet state. For the reaction initiated by benzophenone, only the products of triplet origin will be found as the result of the coupling between the R–$\dot{C}$HOH, R–$\dot{C}$=O and R$^{\cdot}$ radicals.

Thus, under the above experimental conditions, irradiation of benzophenone and butanal at 366 nm leads to the formation of the products expected from the triplet state: butanol, heptan - 4 - one, heptan - 4 - ol, octane - 4,5 - dione and octan - 4 - ol - 5 - one. The observed quantum yields (Table 2) do not differ fundamentally from the ones deduced for the triplet state by quenching by dienes the formation of the products in the direct irradiation of butanal (in the absence of benzophenone). Consequently, the process (B) suggested above does readily occur. Yet, the values are not always reproducible from one set of experiments to another one and the quantum yields vary up to 40%. This divergence is too large to be attributed to experimental errors. In one particular experiment, for example, octane - 4,5 - dione constituted almost half of the products formed under identical conditions. Out of all the obtained results, one observes a net decrease in the formation of heptan - 4 - ol as compared to the other products (its quantum yield, 0.03, does not reach by far the value, 0.11, obtained from the triplet state under direct irradiation conditions).

Considering that the formation of all the compounds, butanol excepted, involves two aldehyde molecules, the quantum yield for disappearance of butanal is 0.56 (somewhat lower to the value 0.74 reached for the triplet reaction by direct irradiation of butanal itself in the absence of benzophenone).

Thus, the radical H exchange reaction (B) is involved in order to reform the benzophenone molecule and to transform a butanal molecule into a Pr–$\dot{C}$HOH radical. As was already pointed out, this chain-like reaction is similar to that observed for mixtures of substituted benzophenones and benzhydrols,[34] the mechanism of which has been rationalized recently.[35] If such an exchange reaction was the only one to occur here, then the concentration of benzophenone would not vary very much. Yet, this is not actually the case since the quantum yield for disappearance of benzophenone is higher than unity (1.4), benzpinacol being formed during the irradiation. Since both reactions (formation of benzpinacol and of a species resulting from a self-quenching type reaction of butanal) take place, several radical processes must be involved. A possible mechanistic rationale could be reaction (D) between a ground state benzophenone molecule and an active species such as a propyl radical formed by decarbonylation of the butyryl radical (reaction C).

$$CH_3{-}CH_2{-}CH_2{-}\dot{C}{=}O \longrightarrow CH_3{-}CH_2{-}\dot{C}H_2 + C{=}O \tag{C}$$



(D)

Although this hydrogen transfer would be favorable, since five-membered ring transition states are usual in radical reactions,[36] we have no direct proof that such a reaction occurs.

The fact that the products (R–CHOH–CO–R, R–CO–R, R–CO–CO–R) containing the butyryl radical R–$\dot{C}$=O form two thirds of the compounds originating from butanal are indicative of the importance of reaction (A). On the other hand, compounds R–CHOH–CO–R and

R–CHOH–R bring experimental proof of reaction (B). As the formation of benzpinacol constitutes an important process ($\phi = 1.4$), another reaction must occur which has not yet been characterized. Further studies on these radical reactions should be undertaken.

EXPERIMENTAL

IR spectra have been obtained with a Perkin Elmer 357 model; UV spectra have been recorded on a Varian Techtron 635 model; the NMR spectra of the products formed in the self-quenching process have been obtained on a Varian EM 360 apparatus: vapor phase chromatography (vpc) has been carried out with a Varian-Aerograph 90P4 model for semi-preparative purpose and with a HI-FI 1400 model for analytical measurements (columns are 10 feet long and contain chromosorb W impregnated with 30% and 15% carbowax respectively).

Materials. The aldehydes are all commercially available. They have been carefully distilled in the case of preparative irradiations. For photophysical purposes the aldehydes have been first purified by VPC then distilled under nitrogen.

Irradiation—general procedure. The photochemical studies were performed employing a Philips HPLN 400 medium pressure mercury arc in a Vycor watercooled jacket. Small scale solutions in Pyrex tubes were degased by four pumping and freezing cycles on a high vacuum line and sealed. These tubes were used for quantum yield measurements with a classical "merry-go-round" apparatus.[37] The 313 nm mercury line was isolated according to Ref. [37]. Large-scale irradiations for preparing the products of the self-quenching process of **3** and **6** were carried out with the same lamp using all the light transmitted by a Vycor glass. The aldehyde, 0.5 molar in pentane solution is continuously bubbled through with N_2 gas for the irradiation period.

Quantum yields. Quantum yields for products formation (singlet and triplet origin) have been obtained by simultaneous irradiation of degassed 0.2 molar pentane solution of the aldehydes with 4,4-dimethylcyclohexanone taken as standard;[21] the solns were adjusted to the same optical density.

The percentages of the formed products were deduced from the integrated areas of the corresponding VPC peaks with a Varian CDS 101 electronic integrator; the results were corrected in order to take into account the difference in response of the flame ionization detection to the various products.

The quantum yields for products formation from singlet origin have been determined in degassed soln 0.05 molar in 2,5 - dimethyl - 2,4 - hexadiene for **2** and **3** (0.11 M for **6**) or 0.02 molar in 1-methylnaphthalene (for **2** and **3**).

Relative intersystem crossing quantum yields have been measured for aldehydes **1** to **8** using the sensitized isomerization of *cis*-piperylene[13] in pentane solution. Analysis were carried out on a 3 meter 15% β, β'-oxydipropionitrile on Chromosorb W column at room temp. Exact quantum yields could be obtained for aldehydes **1**, **2**, **3** and **6** by measuring the amount of triplet quenched (99%, 99%, 97% and 90% respectively) under the experimental conditions: pentane soln 0.2 M in aldehyde and 0.11 M in *cis*-piperylene. 4,4-Dimethylcyclohexanone (ϕ_{isc} = 0.93[21]) was taken as reference. The obtained values are given in Table I.

Laser flash photolysis. Laser flash photolysis experiments were performed at room temp on an apparatus built by Bensasson *et al.*[38] The excitation flash emitted by a neodynium doped laser (VD 230, Compagnie Générale d'Electricité) after two frequency doublings consists of up to 100 mJ of 265 nm radiation having a half-peak height pulse duration of 35 ns. As small amount (10%) of this U.V. light is deflected onto an ITT diode (F 4000, rise time 0.5 ns) for monitoring, the output being displayed on a Tektronix 556 dual beam oscillator. The same oscilloscope recorded simultaneously, via a Radiotechnique photomultiplier (150 UVP, rise time 3 ns), the changes in the analyzing light intensity, passing through the reaction vessel, caused by the laser flash. The transient absorption is analyzed with a Xenon flash (3 kV, 225 μF) triggered in such a way that its maximum intensity occurs at the time of the laser pulse. The analyzing light flash was resolved using a grating monochromator (HUET M 25) before entering the photomultiplier. The analyzing light intensity was constant to within 1% for more than 20 μs over the 300–600 nm wavelength range. The reaction vessel consisted of a 1 × 1 × 3 cm quartz cell filled with the solution and deaerated by bubbling N_2; a fresh sample is used for each pulse.

Transient optical densities were normalized to correct for variation in excitation intensity as pointed out already; the detection system is able to measure absorbance as small as 3×10^{-4}.

Irradiation of butalan **2** *at* 313 nm. Most of the compounds formed during the irradiation of butanal at 313 nm are well-known; the IR and NMR spectra of the isolated products are identical to that given in the Aldrich Library (2nd Edn 1975) of IR and NMR Spectra: BuOH [ref 1300E and 79D (vol. I)]; 4-heptanol [68H and 87C (vol. I)]; 4-heptanone [217B and 108C (vol. II)]; cyclobutanol (88B) and 4-octanone [218F and 110A (vol. II)]. An authentic sample of octan - 4 - ol - 5 - one has been synthesized[39] and oxidized by CrO_3 into octane - 4,5 - dione for comparison with the samples separated from the irradiation mixture.

Irradiation of pentanal **3** *at* 313 nm. *n*-Pentanol [64E and 80A (vol. I)], nonan - 5 - ol (69G) and nonan - 5 - one [219A and 110C (vol. II)] obtained from the irradiation of **3** have identical IR and NMR spectra to that given by the Aldrich Library of IR and NMR spectra (2nd Edn, 1975). The IR and NMR spectra of 2-methylcyclobutanol are identical to that published by Julia *et al.*[40] Decan - 5 - ol - 6 - one is known[41] already as well as decane - 5,6 - dione.[42] We have verified that the chromic oxidation of the α-ketol of photochemical origin gives the same product as the isolated α-diketone.

Irradiation of isobutanal **6** *at* 313 nm. 2-Methyl propan - 1 - ol (66B), 2,4 - dimethylpentan - 3 - ol [72A and 91B (vol. I)] as well as 2,4 - dimethylpentan - 3 - one [215B and 106D (vol. II)] are described in the Aldrich Library (2nd Edn, 1975) of IR and NMR spectra. The structure of the other two dimeric products isolated in the photochemical mixture, 2,5 - dimethylhexan - 3 - ol - 4- one and 2,5 - dimethylhexane - 3,4 - dione, has been confirmed by independant synthesis: for the α-ketol by acyloin synthesis[39] from ethyl isobutyrate, and for the α-diketone by chromic oxidation of the α-ketol.

Irradiation of benzophenone at 365 nm *in the presence of butanal* **2**. Samples (3 ml) of a pentane soln, 0.5 M in butanal and 0.09 M in benzophenone, were degassed by four pumping and freezing cycles and sealed under vacuum. Irradiations were conducted with a "merry-go-round" with isolation of the 365 nm mercury line.[37] Actinometry was monitored by simultaneous irradiation of degassed 3 ml samples of benzophenone (0.1 M) and benzhydrol (0.2 M) in benzene soln.[43] After irradiation (18% conversion of the actinometer), the mixture is analyzed by vpc as described above, while the actinometry is carried out by measuring the variation of the UV absorption of the 248 nm maximum of benzophenone.[43] The results given in the Table II are an average of at least four measurements. The quantum yield for benzophenone disappearance in the irradiated butanal-benzophenone mixture is determined by the variation of the absorption at 365 nm.

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