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INITIATION OF ALDEHYDE PHOTO-OXIDATION IN THE LIQUID PHASE

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Summary

The oxidation of aldehydes in liquid phase proceeds by a chain radical mechanism which can be initiated by a photochemical process. In this study we report the influence of different macroscopic factors on the photochemical initiation rate (concentration of aldehydes, pressure of oxygen, temperature). The initiation consists in a self-deactivation process of the excited states of the aldehyde, and oxygen only intervenes in a physical process favouring the intersystem transition between the singlet and triplet states of aldehydes. Different products have been studied, the mechanism is always the same, but there is a change in the relative importance of the several processes.

Introduction

The photo-oxidation of aldehydes by molecular oxygen in an inert solvent proceeds by a free radical mechanism with long chains [1 - 3]. The absorption by an aldehyde of a photon with sufficient energy leads to free radicals liable to initiate the chains. However, in photo-oxidation studies of organic products which absorb in the u.v. range (313 and 254 nm radiation mainly) it has been admitted that the formation rate of free radicals was dependent only on the radiation intensity absorbed by the solution.

In fact, it appears that the stationary concentration of electronic excited states of the oxidizable product can be modified by other experimental parameters: concentration of the product, pressure of oxygen above the solution, temperature. Consequently, the rate of initiation of chains which depends on the stationary concentration of electronic excited states will be modified by experimental procedures.

In this paper we report the influence of macroscopic factors on the initiation rate of chains in the photo-oxidation of three aldehydes dissolved in decane and excited at 313 nm: heptanal ($C_6H_{13}CHO$, saturated aldehyde), 2-butenal (C_4H_7CHO, unsaturated aldehyde with conjugated double bonds), benzaldehyde (C_6H_5CHO, aromatic aldehyde).

Quantum yield Φ of formation of free radical chain carriers in the photo-oxidation of aldehydes at 313 nm

Experimental procedure

The oxidation of the aldehydes that we have studied proceeds by a long-chain radical mechanism [1 - 3], and the rate V of photo-oxidation (oxygen consumption rate) is given by:

$$V = (\Phi I_a)^{1/2} \cdot f\left[(RCHO), p_{O_2}, \theta\right] \tag{I}$$

where Φ represents the quantum yield of photochemical initiation and f is a function depending on $(RCHO)$, p_{O_2} and θ, I_a is the radiation intensity absorbed by the pure aldehyde on dissolved in decane, $(RCHO)$ is the aldehyde concentration, p_{O_2} is the pressure of oxygen above the solution and θ is the temperature of the liquid phase.

The oxidation of these aldehydes can be induced by biacetyl $(CH_3COCOCH_3)$ excited at 436 nm in the presence of oxygen [4, 5]. The rate of this induced reaction is given by:

$$V_B = v^{1/2} f\left[(RCHO), p_{O_2}, \theta\right] \tag{II}$$

where v is the initiation rate.

Comparison of V with V_B, for the same values of $(RCHO)$, p_{O_2} and θ leads to:

$$\frac{\Phi I_a}{v} = \left(\frac{V}{V_B}\right)^2 \tag{III}$$

In order to have reference experiments we shall use the following conditions: for heptanal $(RCHO) = 7.45$ mol/l (pure product), $p_{O_2} = 450$ Torr, $\theta = 10\,°C$; for 2-butenal $(RCHO) = 12.3$ mol/l (pure product), $p_{O_2} = 475$ Torr, $\theta = 8\,°C$.

In these particular conditions the expression (III) can be written:

$$\frac{\Phi_0 I_{a_0}}{v_0} = \left(\frac{V_0}{V_{B_0}}\right)^2 \tag{IV}$$

In our induced oxidation experiments, the biacetyl concentration was 0.46 mol/l.

We note that benzaldehyde has been already studied by Bäckström *et al.* [3] who have directly determined the initiation rate (study of the formation of higher molecular weight products).

If the excitation conditions of the aldehyde are kept identical $(I_a = I_{a_0})$, from expressions (III) and (IV) we deduce:

$$\frac{\Phi}{\Phi_0} \cdot \frac{v_0}{v} = \left(\frac{V}{V_0} \cdot \frac{V_{B_0}}{V_B}\right)^2 \tag{V}$$

The initiation rate of the induced reaction can be considered as independent of $(RCHO)$ and p_{O_2} [4, 5], so that:

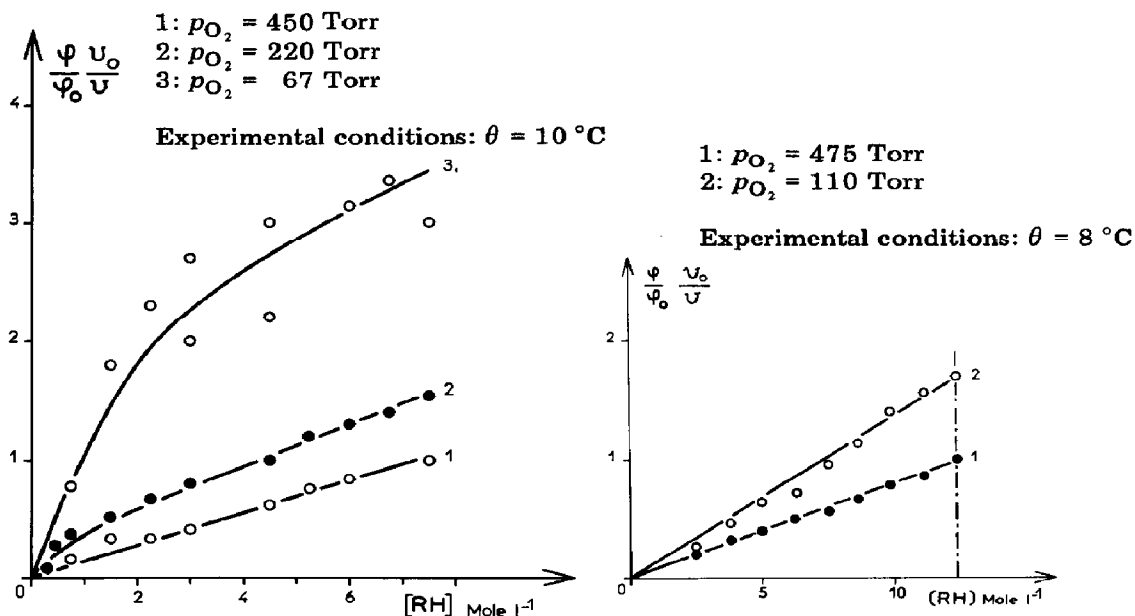$$\frac{\Phi}{\Phi_0} \cdot \frac{v_0}{v} = \frac{\Phi}{\Phi_0} \tag{VI}$$

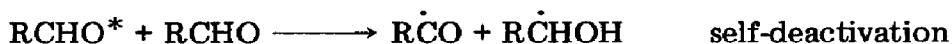Fig. 1. Variations of (Φ/Φ_0) (v_0/v) vs. (RH) for heptanal.

Fig. 2. Variations of (Φ/Φ_0) (v_0/v) vs. (RH) for 2-butenal.

Effect of the aldehyde concentration

In Figs. 1 and 2 we have represented the variations of Φ/Φ_0 as a function of the aldehyde concentration for different oxygen pressures in the case of heptanal and 2-butenal.

We observe that Φ increases with the aldehyde concentration. Besides, when the concentration decreases, in the limit, Φ reaches a value different from zero, so we can exclude as an initiation process the deactivation of electronically excited molecules by oxygen or by dissociation of the excited molecule (Norrish type I for instance).

The only process consistent with our experimental results is a self-deactivation of the excited molecule RCHO* by a molecule in its ground state RCHO:

$$\text{RCHO}^* + \text{RCHO} \longrightarrow \text{R}\overset{\bullet}{\text{C}}\text{O} + \text{R}\overset{\bullet}{\text{C}}\text{HOH} \qquad \text{self-deactivation}$$

where the free radical R$\overset{\bullet}{\text{C}}$O is a chain carrier.

This process has been already proposed by Bäckström et al. [3] in the case of benzaldehyde (measurement of the high molecular weight products formed in the photo-oxidation). But these authors have not observed any effect of the benzaldehyde concentration, in the concentration range studied; the self-deactivation process remains the main process of disappearance of the excited benzaldehyde molecule.

However, in the case of heptanal and 2-butenal, it appears that there is a competition between the self-quenching process and other processes (deactivation by oxygen, unimolecular reaction giving products, non-radiative transition, etc.), and the increase of concentration favours the initiation process.
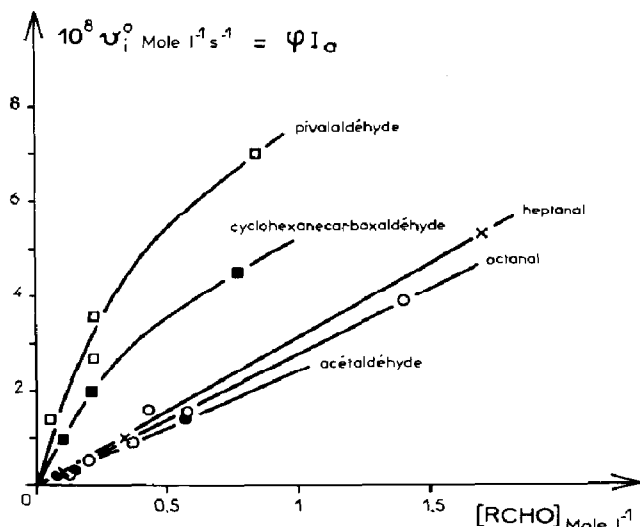
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Fig. 3. Initiation rate for different aldehydes at 0 °C in chlorobenzene. [From G. E. Zaikov, J. A. Howard and K. U. Ingold, Can. J. Chem., 47 (1969) 3017.]
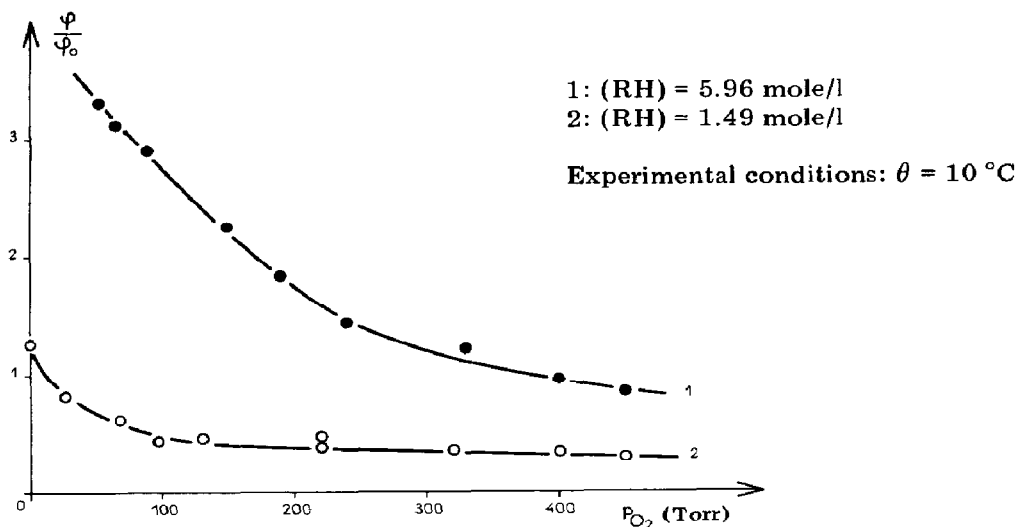

1: (RH) = 5.96 mole/l
2: (RH) = 1.49 mole/l

Experimental conditions: $\theta = 10\,°C$

Fig. 4. Variations of Φ/Φ_0 vs. p_{O_2} for heptanal.

In Fig. 3 we have reported the results obtained by Ingold *et al.* [6] for the photo-oxidation of different aldehydes dissolved in chlorobenzene. Their results are quite similar to ours.

Effect of oxygen concentration

In Figs. 4 and 5 we have plotted the variations of Φ/Φ_0 as a function of oxygen pressure** for different aldehyde concentrations in the case of heptanal and 2-butenal.

** The concentration of oxygen dissolved in the solution depends on the oxygen pressure above the liquid phase according to Henry's law.
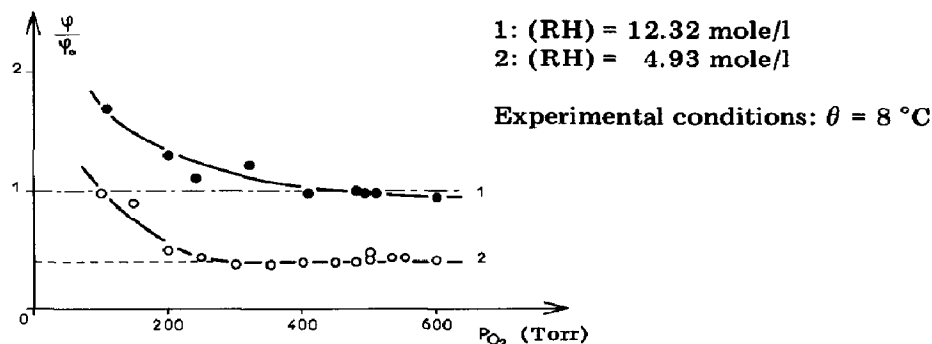
Fig. 5. Variations of Φ/Φ_0 vs. p_{O_2} for 2-butenal.

TABLE 1

Aldehyde	(RCHO) (mol/l)	p_{O_2} (Torr)	Activation energy (kcal/mol)
heptanal	7.45	450	~8
2-butenal	4.9	475	~0
2-butenal	12.3	110	~0

It appears that Φ decreases when the oxygen pressure increases.

This fact emphasizes that initiation cannot be represented only by process (1), because under these conditions Φ would not depend on the oxygen pressure.

Effect of temperature

Further, experiments show that Φ can increase or decrease with the temperature. These effects are shown in Table 1.

Estimation of initiation quantum yield Φ_0 (reference quantum yield)

We have shown above that:

$$\frac{\Phi_0 I_{a_0}}{v_0} = \left(\frac{V_0}{V_{B_0}}\right)^2 \tag{IV}$$

For benzaldehyde (indicated by Bz), we have:

$$\frac{\Phi_0^{Bz} I_{a_0}}{v_0} = \left(\frac{V_0^{Bz}}{V_{B_0}^{Bz}}\right)^2 \tag{VII}$$

Then, we can write:

$$\Phi_0 = \Phi_0^{Bz} \left(\frac{V_0}{V_{B_0}} \cdot \frac{V_{B_0}^{Bz}}{V_0^{Bz}}\right)^2 \tag{VIII}$$

If we accept the value Φ_0^{Bz} determined by Bäckström and Riiner [3] we can calculate Φ_0. The results are given in Table 2.

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TABLE 2

Estimation of Φ_0

Aldehyde	(RCHO) (mol/l)	p_{O_2} (Torr)	θ(°C)	V_0/V_{B_0}	Φ_0
benzaldehyde	10	450 475	10	0.63	1 [3]
heptanal	7.45	450	10	0.306	~0.2
2-butenal	12.3	475	10	0.1	~0.01

Intervention of singlet and triplet states in the initiation processes

Inhibition of photo-oxidation by naphthalene

Naphthalene can deactivate the triplet state T_1 of the aldehyde by electronic energy exchange transfer: the naphthalene triplet state energy is 61 kcal/mol against 70 to 80 kcal/mol for the aldehyde triplet state energies.

On the other hand, naphthalene can neither deactivate the singlet state S_1 of aldehyde nor cause a "secondary inhibition" by reacting with chain carrier free radicals resulting from the oxidation of aldehydes. For instance, the thermal oxidation rate of heptanal is not modified on addition of naphthalene.

Thus the addition of naphthalene allows us to study the participation of the triplet state T_1 in the initiation process of this photo-oxidation.

Figures 6, 7 and 8 show the variations of V_N/V as a function of naphthalene concentration, V_N representing the photo-oxidation rate in the presence of naphthalene.

Let us denote by Φ_S and Φ_T the quantum yields of initiation from the singlet state S_1 and triplet state T_1 respectively. When naphthalene is not present we can write:

$$V = (\Phi_S + \Phi_T)^{1/2} . I_a^{1/2} . f (p_{O_2}, (RCHO), \theta) \tag{IX}$$

as $\Phi_S + \Phi_T = \Phi$

When the naphthalene concentration increases indefinitely, in the limit V_N rate reaches the following value:

$$(V_N)_{(N)=\infty} = (\Phi_S)^{1/2} . I_a^{1/2} . f (p_{O_2}, (RCHO), \theta) \tag{X}$$

The relative participation of singlet and triplet states can then be written:

$$\frac{\Phi_S}{\Phi_T + \Phi_S} = \left(\frac{V_N}{V}\right)^2_{(N)=\infty} \qquad \frac{\Phi_T}{\Phi_S + \Phi_T} = 1 - \left(\frac{V_N}{V}\right)^2_{(N)=\infty} \tag{XI}$$
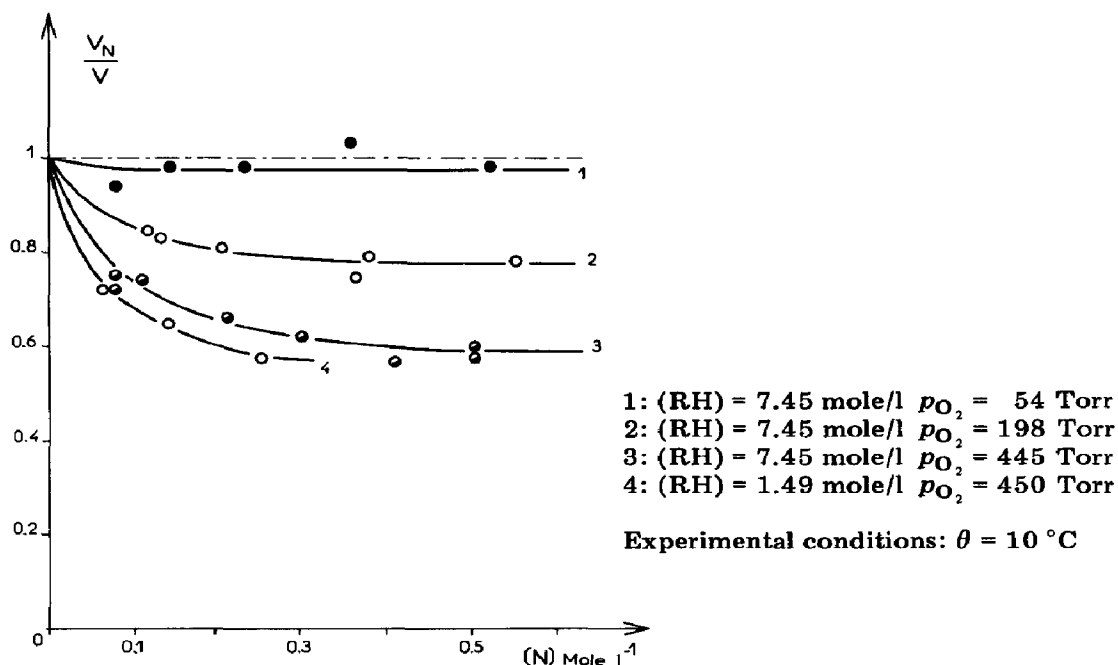
The resulting values are given in Table 3.

Fig. 6. Effect of naphthalene on the photo-oxidation rate of heptanal.

1: (RH) = 7.45 mole/l p_{O_2} =   54 Torr
2: (RH) = 7.45 mole/l p_{O_2} = 198 Torr
3: (RH) = 7.45 mole/l p_{O_2} = 445 Torr
4: (RH) = 1.49 mole/l p_{O_2} = 450 Torr

Experimental conditions: θ = 10 °C

1: p_{O_2} = 465 Torr
2: p_{O_2} = 110 Torr

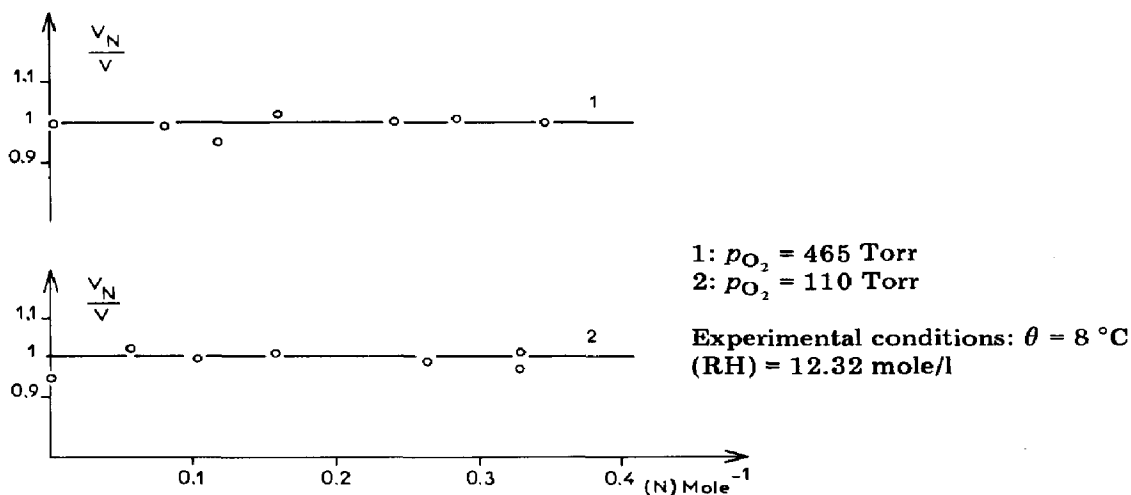Experimental conditions: θ = 8 °C
(RH) = 12.32 mole/l

Fig. 7. Effect of naphthalene on the photo-oxidation rate of 2-butenal.

Relative participation of triplet state in the initiation

In the case of 2-butenal we observe that only the singlet state produces initiation. However, in the case of benzaldehyde we observe a very important participation of the triplet state, in agreement with the results reported by Bäckström *et al.* [3] who exclusively assign initiation to the triplet state.

The case of heptanal appears as intermediate between these two limiting cases.
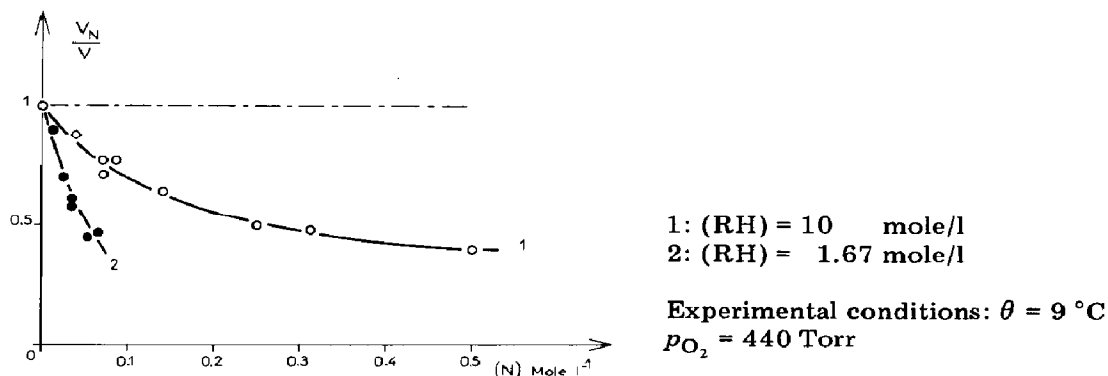
Fig. 8. Effect of naphthalene on the photo-oxidation rate of benzaldehyde.

TABLE 3

Relative participation of singlet and triplet states in the initiation

Aldehyde	Experimental conditions			Contribution of the singlet state and the triplet state to the initiation	
	(RCHO) (mol/l)	p_{O_2} (Torr)	Temperature (°C)	Φ_S/Φ	Φ_T/Φ
2-butenal	12.32	110	8	1	0
	12.32	465	8	1	0
heptanal	7.45	54	10	~0.95	~0.05
	7.45	198	10	~0.60	~0.40
	7.45	445	10	~0.35	~0.65
	1.49	450	10	~0.30	~0.70
benzaldehyde	10	440	9	<0.10	>0.90*
	1.67	440	9	<0.10	>0.90*
benzaldehyde [3]	10	760	18	0	1

* The naphthalene interferes in the absorption, so it was not possible to reach sufficient naphthalene concentrations in order to get the inhibition limit.

In fact, the participation of the triplet state is variable; in particular it increases with the oxygen pressure.

Figure 9 represents the variations of Φ_T/Φ_0, Φ_S/Φ_0 and Φ/Φ_0, ($\Phi = \Phi_S + \Phi_T$) as a function of oxygen pressure.

We observe that Φ_S decreases when p_{O_2} increases, so oxygen gives rise to a deactivation process for the S_1 state, and this process does not directly lead to the formation of chain carrier free radicals. On the contrary, Φ_T increases with p_{O_2}, and this fact can be assigned to: a yield of formation of chain carrier free radical $R\dot{C}O$, as a result of T_1 increasing with oxygen pressure; an increase of the quantum yield for population of triplet state.

The first assumption can be excluded, because, in this case, the triplet state T_1 should give rise to an attack process by oxygen leading to the for-
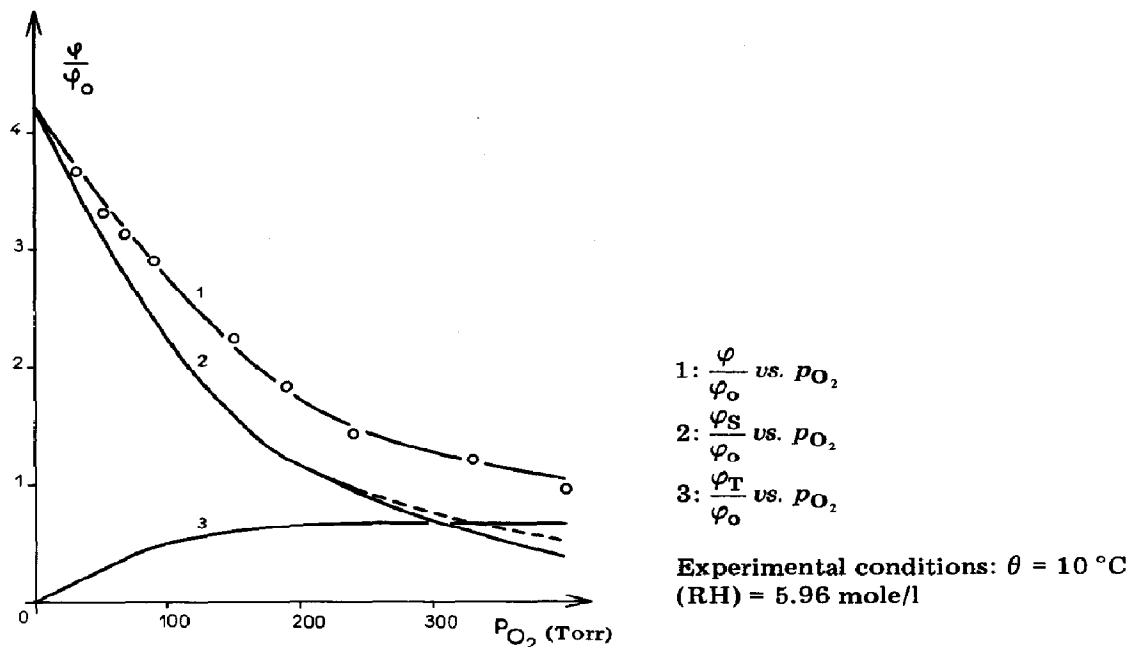
Fig. 9. Variations of (Φ/Φ_0), (Φ_S/Φ_0), (Φ_T/Φ_0) vs. p_{O_2} for heptanal.

mation of RĊO with a yield comparable with the one of other processes (self-deactivation) where oxygen does not interfere. But, for high oxygen pressure, when the participation of the triplet state is important $(\Phi_T/(\Phi_T + \Phi_S) \simeq 2/3)$ we observe (see Fig. 1) that the global yield Φ reaches zero when the concentration decreases, so that the self-deactivation process is always the main process for formation of RĊO, and oxygen does not directly participate in an initiation process.

On the other hand, our experimental results are easy to interpret if we assume the existence of a perturbation by oxygen of the intersystem transition of the population state T_1 according to:

$$S_1 + O_2(^3\Sigma_g^-) \longrightarrow T_1 + O_2(^3\Sigma_g^- \text{ or } ^1\Delta_g)$$
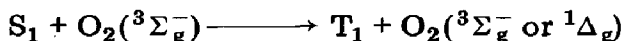
We have also checked that singlet oxygen, which may be produced, was not liable to lead to the initiation of the photo-oxidation; in fact the photo-oxidation sensitized with methylene blue gives a negative result. [N.B. In the case of 2-butenal we also observe an important inhibition of the initiation by oxygen (see Fig. 2). As in the case of heptanal the oxygen reacts on the singlet state without giving rise to the formation of chain carrier free radical. However, the kind of inhibition process cannot be specified in this case.]
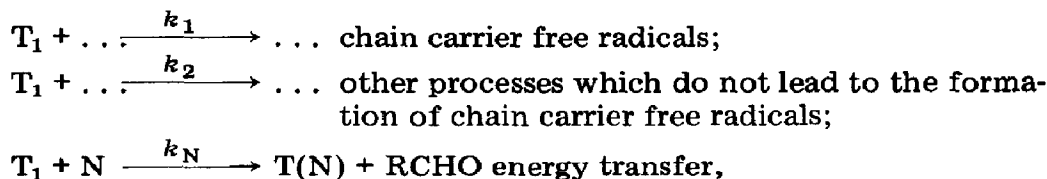
Estimation of the lifetime τ of triplet state T_1 precursors of free radicals

Electronic energy transfer between triplet state of aldehyde and naphthalene accounts for the observed inhibition. If l stands for the relative participation of aldehyde triplet state in the initiation ($l = (V_N/V)^2_{(N) = \infty}$, for in-

finite concentration of naphthalene), then it is possible to estimate the life-time of this state by plotting the variations of:

$$\frac{l\,V^2}{V_N^2 - (1-l)\,V^2} \quad \text{or} \quad \frac{l}{\left(\dfrac{V_N}{V}\right)^2 - (1-l)} \quad vs. \text{ (N)}$$

The deactivation mechanism of T_1 may therefore be represented by:

$$T_1 + \ldots \xrightarrow{\ k_1\ } \ldots \text{ chain carrier free radicals;}$$

$$T_1 + \ldots \xrightarrow{\ k_2\ } \ldots \text{ other processes which do not lead to the forma-}$$
$$\text{tion of chain carrier free radicals;}$$

$$T_1 + N \xrightarrow{\ k_N\ } T(N) + RCHO \text{ energy transfer,}$$

where $T(N)$ represents the triplet state of naphthalene and RCHO the ground state of aldehyde.

If v^T is the initiation rate from T_1, and v_N^T the same rate in the presence of naphthalene, then:

$$\frac{v_N^T}{v^T} = \frac{1}{1 + [k_N/(k_1 + k_2)]\,(N)} \tag{XII}$$

and

$$\frac{v^T}{v_N^T} = \frac{l\,v^2}{v_N^2 - (1-l)\,v^2} = 1 + \frac{k_N}{k_1 + k_2} = 1 + k_N\,\tau\,(N) \tag{XIII}$$

Figures 10 and 11 represent the variations of v^T/v_N^T as a function of (N) (Stern–Volmer plots).

If we assume that the rate of the energy transfer process is limited by diffusion, then, from the slope determination of the straight line obtained, it is possible to estimate the value τ of the lifetime of the triplet state which is the precursor of free radicals. These results are reported in Table 4. (N.B. In the case of benzaldehyde, Φ_T is practically constant [3]. When benzaldehyde is diluted six times we estimate that the lifetime τ of the triplet state is about 5.5 times longer (see Table 4). This result implicates that the self-deactivation process:

$$RCHO\ (T_1) + RCHO \longrightarrow R\dot{C}O + R\dot{C}HOH$$
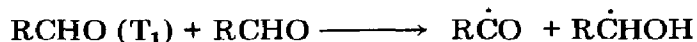
is the main deactivation process of the triplet state of benzaldehyde. Using a different technique this result corroborates the previous results published by Bäckström and Riiner [3].
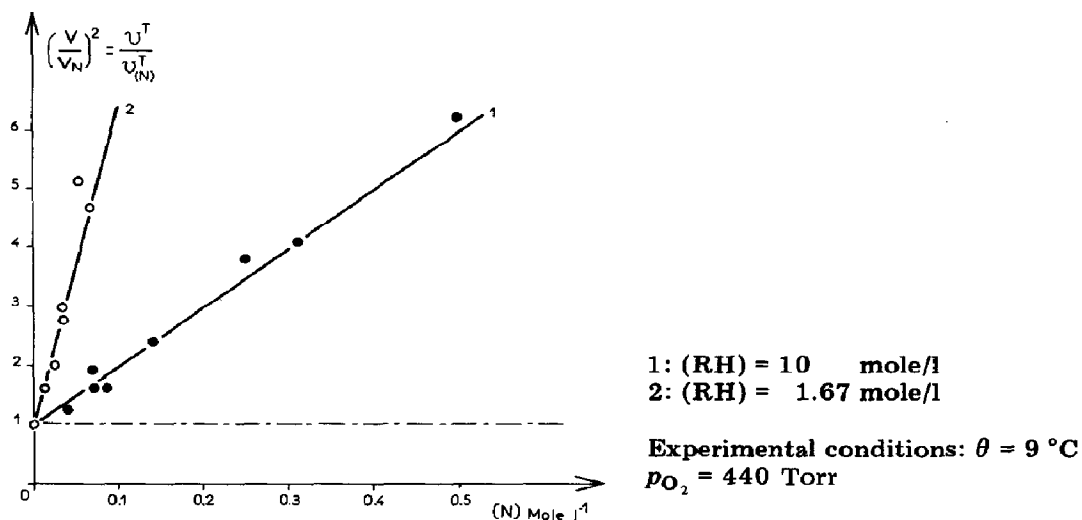
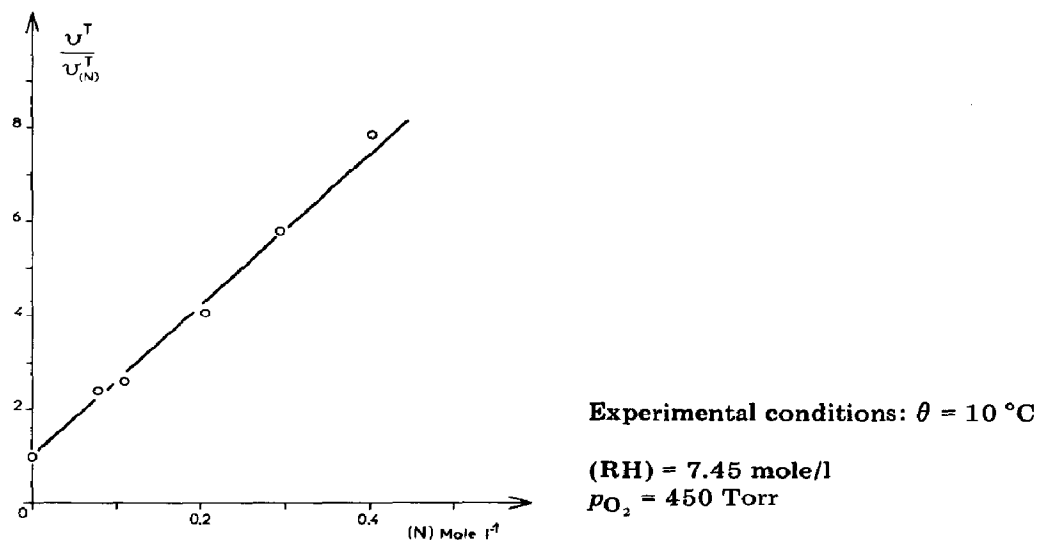Fig. 10. Inhibiting effect of naphthalene on the photo-oxidation of benzaldehyde (Stern–Volmer plots).

1: (RH) = 10   mole/l
2: (RH) =   1.67 mole/l

Experimental conditions: θ = 9 °C
p_{O_2} = 440 Torr

Experimental conditions: θ = 10 °C

(RH) = 7.45 mole/l
p_{O_2} = 450 Torr

Fig. 11. Inhibiting effect of naphthalene on the photo-oxidation of heptanal (Stern–Volmer plots).

TABLE 4

Aldehyde	(RCHO) (mol/l)	p_{O_2} (Torr)	θ (°C)	l	$\tau \times 10^9$ (s)
heptanal	7.45	450	10	0.75	5
2-butenal	12.32	465	10	0	—
benzaldehyde	10	440	9	1	2
	1.67	440	9	1	11
	10	760	18	1	3 [3]

Conclusion

The initiation of the photo-oxidation of aldehydes is mainly due to a self-deactivation process of the excited states RCHO* leading to the formation of chain carrier free radicals RĊO:

$$RCHO^* + RCHO \longrightarrow R\dot{C}O + R\dot{C}HOH$$

This self-deactivation mainly affects the excited singlet states S_1 (2-butenal), triplet states T_1 (benzaldehyde), or both singlet and triplet states S_1 and T_1 (heptanal).

Oxygen does not intervene in the initiation process but is liable to perturb the $S_1 \rightarrow T_1$ transition which populates the triplet state T_1 (heptanal). In this case, the participation of this state in the initiation of oxidation chains increases when the concentration of oxygen dissolved in the solution increases.

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