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Laser Spectroscopy of Substituted Benzophenone Used as Photo-Initiators of Vinyl Polymerization

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Summary

Nanosecond laser spectroscopy is applied to the determination of the rate constants of several processes involved in the photochemistry of a series of substituted benzophenones. The results allow the initiation of a vinyl monomer polymerization to be discussed and reveal a peculiarity of the benzene/THF system.

1 - Introduction

In the previous paper of this series [1], we reported on a laser spectroscopy investigation of the excited states of benzophenone in the presence of amine. Then we correlated the results with the data obtained in photopolymerization experiments under steady state conditions [1]. We wish now to complete these results by an investigation of several substituted benzophenones and of the role of THF in the initiation mechanism.

2 - Experimental

The irradiation procedure and the laser spectroscopy device have been described in ref.1.

3 - Results and discussion

a) Laser spectroscopy investigation

The photochemistry of benzophenone has been extensively investigated for a long time [2] in aprotic solvents and in protic media such as alcohols. However, it seems interesting to investigate the photoreduction of the triplet state by THF : one actually observes a decrease of the triplet state lifetime at low THF concentrations [k_q = $(4.2\pm0.6)\times10^6$ $M^{-1}.s^{-1}$]. With higher concentrations, the Stern-Volmer plot does not remain linear (Fig.1). The same observation is deduced when

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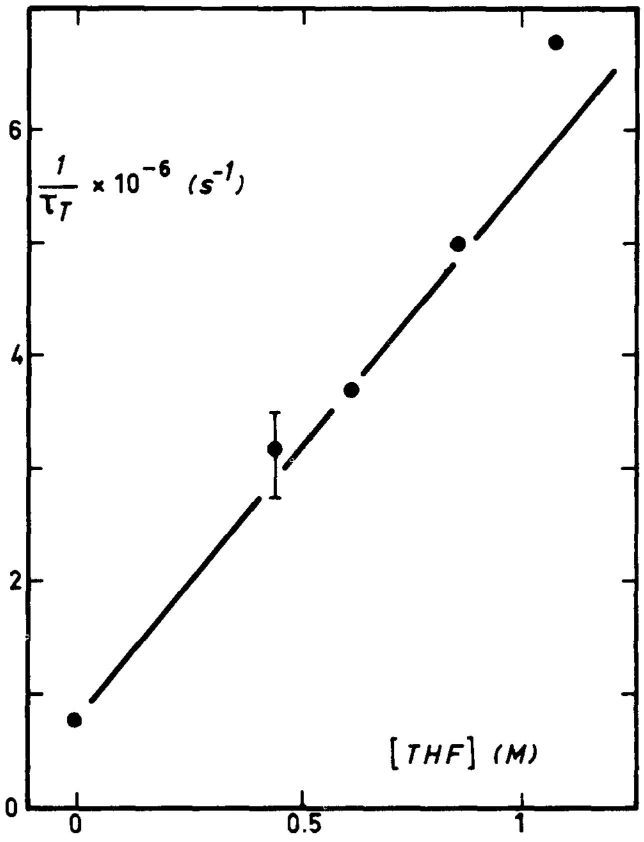


Fig.1 : Stern-Volmer plot for the quenching of the triplet state of benzophenone by THF.

the optical densities of the ketyl radical (Fig.2) are displayed as stated in eq.1. It can be shown that the quenching of the triplet state by THF leads only to ketyl and THF radicals, establishing thus, the chemical nature of the quenching by THF ; this statement remains valid up to [THF] = 2 M.

$$\begin{tikzcd}
{}^{3}\mathrm{BP} \arrow[r, "k_d"] \arrow[dr, "\mathrm{THF}", "k_q"'] & {}^{0}\mathrm{BP} \\
& \mathrm{K}^{\bullet} + \mathrm{THF}^{\bullet}
\end{tikzcd}$$

$$\frac{1}{\mathrm{OD}_K} \propto 1 + \frac{k_d}{k_q[\mathrm{THF}]} \qquad \text{(eq.1)}$$

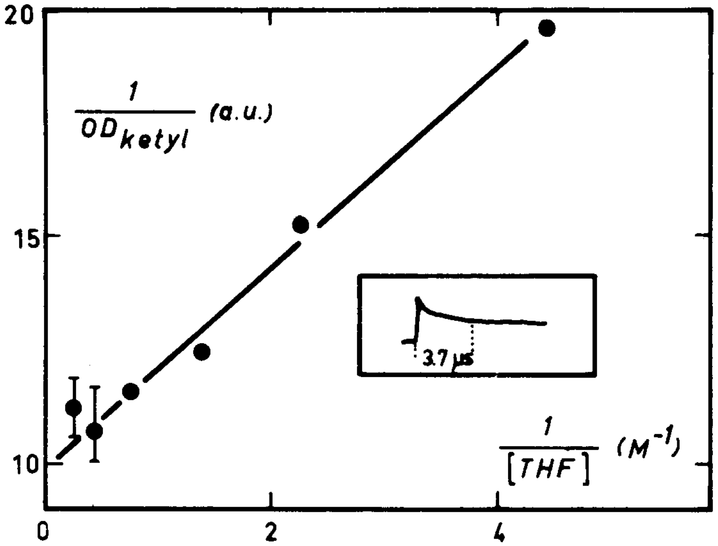


Fig.2 : Stern-Volmer plot for the appearance of the ketyl radical of benzophenone as a function of the THF concentration.

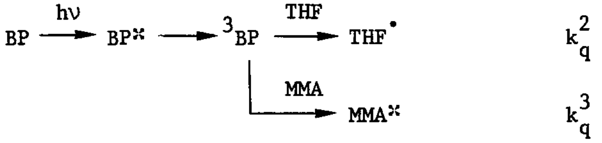
	τ_T^{air} (ns)	τ_T^0 (μs)	$k_q^{MMA} \times 10^{-7}$ $(M^{-1}.s^{-1})$	$k_q^{THF} \times 10^{-6}$ $(M^{-1}.s^{-1})$
BP	200	1.3	6.6	4.5
4-Cl	210	1.3	5.2	6.4
4-OCH_3	125	1	9.1	2.5
4-F	185	1.4	9.9	5.6
4-COOH	240	1.2	5.4	4.3
4,4'-CH_3O	125	1.5	23	-

Table 1 : Triplet state lifetimes of various benzophenones in benzene solution in the presence (τ_T^{air}) or in the absence of oxygen (τ_T^0) and bimolecular quenching rate constants by THF and MMA.

Similar experiments have been carried out upon substituted benzophenones (Tab.1). The same type of behaviour is observed. In addition, we have measured the rate constant of the bimolecular quenching of the triplet state by MMA which is detrimental to the initiation efficiency of the polymerization.

b) Steady state polymerization

The rate of the polymerization of MMA initiated by these molecules can be easily expressed by eq.3 (α is the initiation coefficient of the THF radical), according to the scheme (eq.2).



$$BP \xrightarrow{h\nu} BP^{*} \longrightarrow {}^{3}BP \xrightarrow{THF} THF^{\bullet} \quad k_q^2 ; \qquad {}^{3}BP \xrightarrow{MMA} MMA^{*} \quad k_q^3 \qquad \text{(eq.2)}$$

$$R_p = \frac{k_p}{k_t^{1/2}} [MMA] \sqrt{2.3\ I_0\ OD\ \phi_{ST}\ \alpha\ \frac{k_q^2[THF]}{k_q^3[MMA] + k_q^2[THF]}} \qquad \text{(eq.3)}$$

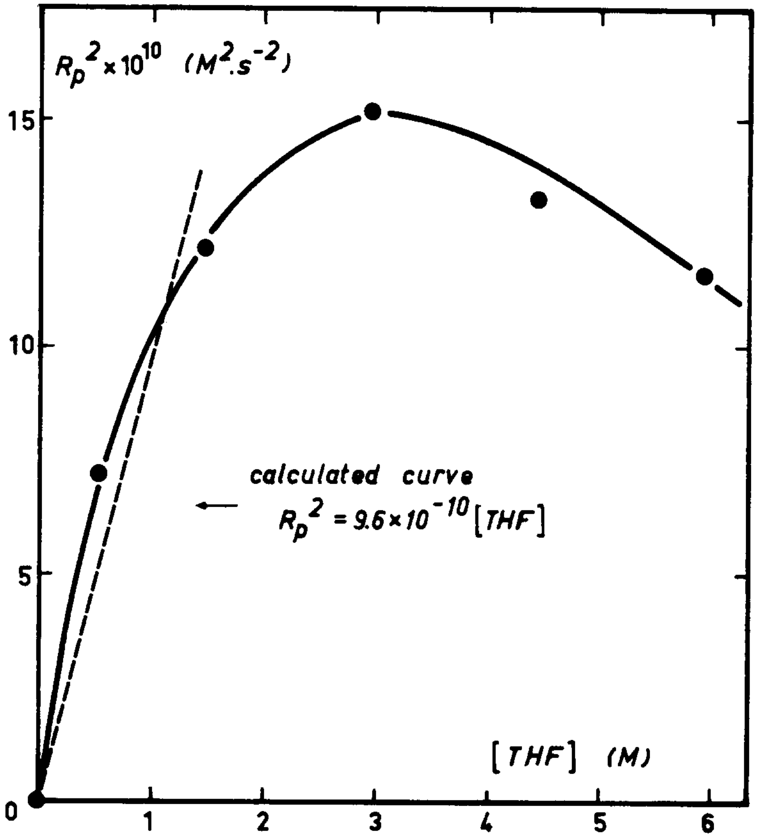


Fig.3 : Rate of the polymerization of MMA induced by benzophenone in benzene-THF. [MMA] = 4.7 M ; $I_0 = 2.5\times10^{16}$ $phot.cm^{-2}.s^{-1}$; OD = 0.15 (λ = 365 nm) ; dotted line : see text.

In the case of benzophenone itself and [MMA] = 4.7 M, R_p^2 would be a linear function of [THF]. This is essentially true (Fig.3) for [THF] $\leqslant$ 2 M, value beyond which the Stern-Volmer plot deviates from linearity. The dotted line of fig.3 is calculated with the value α = 0.057 determined from previous measurements [3]. The curvature of the experimental line shows that chemical reactions are likely to occur with THF radicals, causing a decrease of their concentration. For a part this loss in the initiation mechanism could be due to the formation of an adduct, a reaction which is well established with benzophenone in the presence of alcohols [2]. Moreover, the present result demonstrates that the extrapolation of data obtained at low concentration must be regarded with caution. $THF^{\bullet}$ is reported to behave so in [4].

The rates of polymerization R_p, obtained with various benzophenones are reported in fig.4 and table 2. The same decrease is observed at high THF concentration. In some cases, the values of table 1 allow the rates R_p to be calculated. Table 2 shows a satisfactory agreement

Substituent (X)	$R_p \times 10^5$ (M.s^{-1})	$R_p^1 \times 10^5$ (M.s^{-1}) *experimental*	$R_p^2 \times 10^5$ (M.s^{-1}) *calculated*
4-H	3.6	2.9	3.1
4-Cl	8.1	4.4	4.1
4-F	3.6	3.4	2.9
4-OCH_3	1.9	1.8	1.9
4-NO_2	1.6	-	-
4-NH_2	1.0	-	-
4-COOH	5.9	3.9	3.7
4-ϕ	5.7	-	-
4,4'-OCH_3	1.5	-	-
2-ϕ-CO	3.3	-	-
Mischler's ketone	1.9	-	-
BTD*	8.7	-	-
benzile	5.5	-	-

Table 2 : Rate of polymerization of MMA in pure THF (*column 1*), in benzene-THF ([THF] = 1 M)(*column 2 and 3*). [MMA] = 4.7 M ; I_0 = 2.5×10^{16} phot.cm^{-2}.s^{-1}. * 3,3',4,4'-benzophenone tetracarboxylic dianhydride.

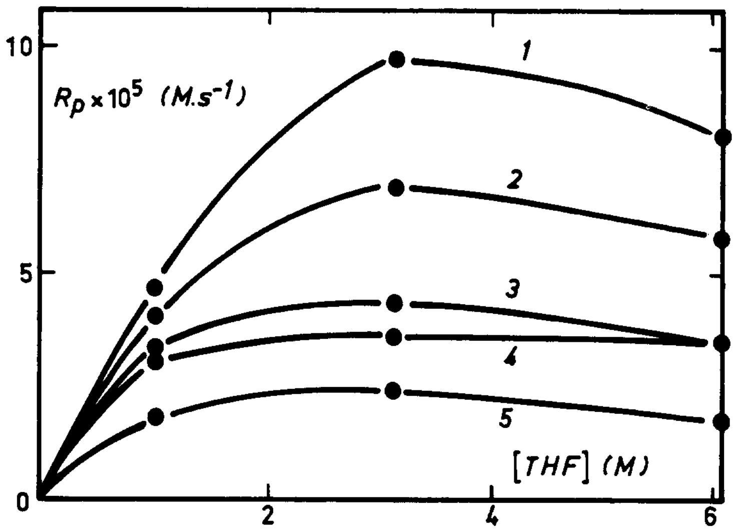


Fig.4 : Rate of polymerization of MMA induced by various benzophenones. Experimental conditions : see fig.3. (*1*) BP-Cl ; (*2*) BP-COOH ; (*3*) BP-F ; (*4*) BP ; (*5*) BP-OCH_3.

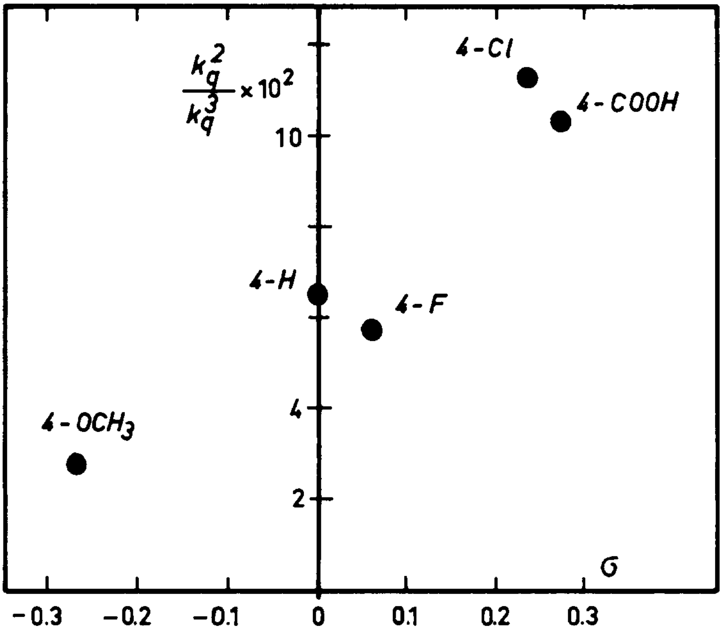


Fig.5 : Efficiency of the initiation process as a function of the Hammett's constants.

between the calculated and the experimental values obtained at low THF concentration. Moreover, table 2 brings out the differences between the relative efficiencies of the initiators in pure THF and in a benzene-THF mixture. This observation is attributed to small changes of the THF initiation coefficient induced by interactions between the THF radical and the initiator. It can also be shown that the ratio k_q^2/k_q^3 which is representative of the initiation efficiency is an increasing function of the Hammett's constants (Fig.5).

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