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DIRECT MEASUREMENTS OF CARBONYL TRIPLET LIFETIME IN THE NANOSECOND RANGE: INVESTIGATION IN A POLYMER SOLUTION

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Summary

A "picosecond" spectroscopy technique allows direct measurements of the carbonyl triplet lifetime τ_T and the intersystem crossing constant K_{ST} of polymers. We thus obtain the primary step of the Norrish type II photodegradation process and our results for the τ_T values are in good agreement with these deduced by Wagner from Stern–Volmer experiments.

Introduction

The Norrish type II reaction in the monoarylketones is one of the most widely studied photochemical processes [1] and results in a chain scission giving a ketone and an olefin. The products are known to arise from the triplet state according to:
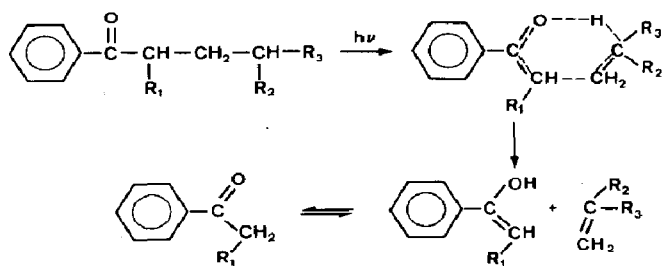
The photodegradation of ketones and polymers in solution has been studied previously almost exclusively through steady-state experiments [2]. The photolysis study resulted in linear Stern–Volmer plots of the type:

$$\frac{\Phi^0}{\Phi} = 1 + \tau_T k_q [Q]$$

where Φ^0 and Φ are respectively the quantum yield of acetophenone production in the absence and presence of quencher, τ_T the lifetime of the carbonyl triplet and k_q the rate constant for the bimolecular quenching.

These kinds of experiments gave values for the term $\tau_T k_q$. They were performed, for example, on valerophenone and polymeric material such as poly(vinyl phenyl ketone) (PVPK) [2]; from several estimates of the order of magnitude of k_q, Wagner [2] was able to show that the transient state appeared in the 1 to 15 ns range. It would be interesting to measure the triplet lifetime directly to obtain a direct value of k_q and to gather information about the primary process of the Norrish type II photodegradation. Some fast kinetic methods had been applied [3, 4] in the sub-microsecond range but no measurement was performed in the 1 - 15 ns time scale.

For several years, a very important development in laser spectroscopy has been observed involving important applications in photochemistry [6 - 13]. Accordingly it is now possible to observe transient lifetimes as short as 10 ps by picosecond spectroscopy. Nevertheless, the time scale lying between about 1 and 10 ns is extremely difficult to investigate: this range corresponds to the lower limit of the photolysis by Q-switched lasers, and to the upper limit of picosecond spectroscopy because of the length of the optical delay. Moreover, many difficulties may appear in this range with the risetime of the detectors.

We have reported recently concerning the application of picosecond spectroscopy for attaining the transient state which is involved in the Norrish II photodegradation process of valerophenone [14]; we used the whole train of pulses of a mode-locked ruby laser simultaneously as a pumping source and as an interrogating beam.

This work allowed us to obtain spectroscopic evidence for the triplet state, studied by Wagner [2] according to Stern–Volmer experiments several years ago and to collect information on this transient state (generation rate constant, lifetime, extinction coefficient). We reported in the same paper, the first result obtained with a polymeric material, poly(vinyl phenyl ketone) (PVPK), in which the photodegradation is assumed to proceed in the same way. However, that paper dealt with lifetimes and generation rate constant measurements, only in the particular case where the overall process studied can take place completely in the interval between two pulses of the excitation train (~ 10 ns). Our purpose is now to study the general case in a wide range of K_{ST} and τ_T values ($K_{ST} > 10^8$ s^{-1} and $2 < \tau_T < 15$ ns) and to present experimental results obtained in the case of valerophenone and PVPK. In particular, the solvent dependence of the non-radiative rate constant can be observed.

Experimental

Materials

All solvents were commercial products of the highest grade. Valerophenone purchased from the Fluka Corp. was used without further purification. PVPK has been prepared by radical polymerization with low conversion (25%), under N_2, with 0.05% of AIBN in benzene at 60 °C. The polymer was reprecipitated several times from its benzenic solution with methanol and dried at 50 °C under vacuum.
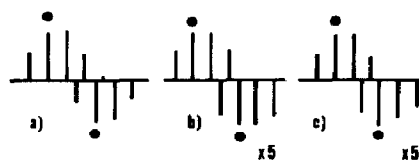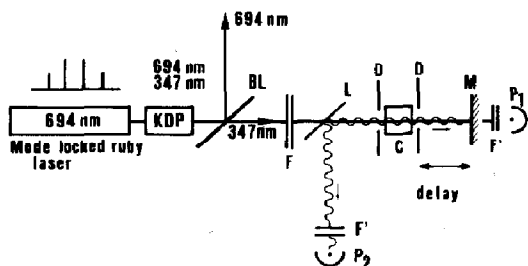
Fig. 1. Experimental set up. BL, beam splitter; F, 694 cut-off filter; L, slab; D, diaphragms; C, sample cell; M, mirror; F', filters; P_1, P_2, photocells.

Fig. 2. Transmitted train of pulses observed on an oscilloscope. (a) solvent; (b) valerophenone; (c) PVPK. The upper and lower trace correspond to the intensity of the interrogating light before and after the sample cell.

Apparatus

The experimental set up is schematically shown in Fig. 1. The beam which serves as pumping source to induce S_0–S_1 transition in the sample A, is simultaneously used as the interrogating beam. This light corresponds to the output of a mode-locked ruby laser: a train of 7 to 8 pulses, 10 ns separated, 300 ps half-duration and λ = 347 nm (obtained by frequency doubling in a KDP crystal). The energy of each pulse lies between 5 and 25 mJ. This light is first directed to the beam splitter (L) and to a cupric sulphate filter, which removes the red light not converted in the KDP crystal, then travels over the sample and is received by the mirror (M) under normal incidence. The weak part of light transmitted by this mirror is collected by the photocell (P_1); the other part returns through the cell (A) and reaches the backface of a slab (L) which directs a part of this light to the photocell (P_2). The experimental procedure involves, for each pulse of the train, the determination of the output ratio of these two cells, first with the excitation beam striking the sample when containing the solvent only (α_0) and then with the solution present (α) (Figs. 2a and 2b). The optical transmission of the sample is given by $T = \alpha/\alpha_0$.

If the distance L between the sample (A) and the mirror (M) is varied, the transmission may be recorded as a function of the optical delay $2L/c$ (c = light velocity), *i.e.* a function of time.

Theoretical investigation and results

Lifetime of the transient state < 4 ns and its formation rate constant > 10^9 s^{-1}

This situation corresponds to the valerophenone triplet. In such a case the kinetic analysis of the transient state may be regarded as follows: the concentration of the valerophenone triplet generated by any one laser pulse decreases according to first-order kinetics:

$$c_T(t) = c_T(0) \exp\left(- t/\tau_T\right)$$

where $c_T(0)$ and $c_T(t)$ are the concentrations of molecules of the triplet state at the end of the excitation process and at the time t and τ_T is the triplet lifetime.

Thus the transmission of the solution can be expressed by:

$$T(t) = \exp[-2.3\,l\,\epsilon_{01}c_0(t) - 2.3\,l\,\epsilon_{TT}c_T(t)]$$

where $c_0(t)$ is concentration of the fundamental singlet state, ϵ_{01} and ϵ_{TT} are extinction coefficients of the S_0–S_1 and T–T transitions at 347 nm, l is optical length of the sample.

However, these populations are assumed to be approximately time independent along the interrogating pulse (*i.e.* the triplet lifetime is long compared to the pulse duration). Of course, these assumptions are not valid while pumping proceeds, that is why no measurements are possible at that moment.

The number of excited molecules is very low in relation to the weakness of S_0–S_1 absorption (ϵ_{01}^{347} #50 M^{-1} cm^{-1}). We can write:

$$T(t) \# \exp[-2.3\,l\,\epsilon_{01}c] \times \exp[-2.3\,l\,\epsilon_{TT}c_T(t)]$$

and

$$\ln\log\frac{T_0}{T(t)} = \ln\,[(\epsilon_{TT}lc_T(0)] - \frac{t}{\tau_T}$$

The study of the experimental results according to this kinetic model accounts for the triplet state of valerophenone benzenic solution ($c = 10^{-2}$ M) (Figs. 3 and 4): $\tau_T = 4 \pm 0.3$ ns; $\epsilon_{TT}^{347} \sim 7 \times 10^3$ M^{-1}cm^{-1}; $K_{ST} > 5 \times 10^{10}$ s^{-1}.

Thus, it becomes possible to account for the shape of the train observed on Fig. 2b. Each pulse of the train generates some molecules in the triplet state, and that in relation to its own energy, but the next one always strikes the sample when the absorption due to the transient is completely relaxed. This is a satisfactory explanation of the experimental results: the train is symmetrically distorted with respect to the central pulse, *i.e.* the higher the energy carried by a single pulse, the lower the transmission. Moreover, the shape of the train shows that we have no accumulation of molecules in a long lived intermediary state which absorbs significantly the 347 nm analysis light.

Any lifetime of state between 1 and 15 ns and any rate of generation constant above 10^8 s^{-1}

We can assume the experimental observations of Fig. 2c to be quite different when the transient lifetime becomes greater than 4 ns or the generation constant, lower than about 3×10^9 s^{-1}. In such cases, the transient state population generated by the first pulse has not completely disappeared when the next one reaches the sample; thus a building up phenomenon takes place and continues as long as the excitation light endures. At this point, the only way to interpret the experimental results is to attempt an overall computer calculation, taking into account all the parameters on which the experimental behaviour may be dependent.
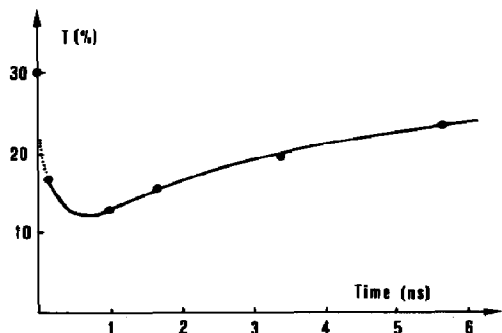
Fig. 3. Experimental transmission as a function of the optical delay $t = 2l/c$ for valerophenone in benzene.
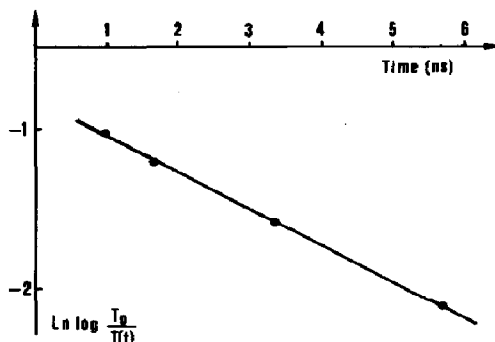
Fig. 4. Plot of ln log T_0/T (t) vs. time for valerophenone.

Let us consider a system made of three levels: two singlet states (fundamental S_0, excited S_1) and a transient state (triplet T). The changes in populations induced by the excitation light may be described by the following equations:

$$\frac{dN_1}{dt} = \sigma_{01}P(t) - \frac{N_1}{\tau}$$

$$\frac{dN_T}{dt} = K_{ST}N_1 - \frac{N_T}{\tau_T} \qquad \text{system (1)}$$

$$N_0 + N_1 + N_T = N$$

where N is total population density (cm^{-3}), N_0, N_1, N_T are population densities in the fundamental, excited singlet and triplet states, σ_{01} is absorption cross-section S_0–S_1 (cm^2) ($\epsilon = 2.6 \times 10^{20}\,\sigma$), $P(t)$ is pumping function (assumed to be $P(t) = P_i\,(t)$ as long as singlet pulse i endures; $P(t) = 0$ between two pulses).

We expect the computer solution of these equations to show the time dependence of the population in three levels: S_0, S_1, T. After the pulse i, we have the populations N_1^i, N_T^i, N_0^i. The probing beam being the same train of pulses separated by 10 ns, the measurement at the time t gives the values of the transmission obtained for each pulse of the train (the time t is now the time required between the excitation and the interrogation of the sample by the pulse i). The values of $N_0(t)$ and $N_T(t)$ are determined by solving, for each pulse, a system of rate equations analogous to system (1) in which the initial conditions are N_0^i, N_1^i, N_T^i and $P(t) = 0$. Hence the transmission may be calculated, at any moment t through the expression:

$$T(t) = \exp[-l\sigma_{01}N_0(t) - l\sigma_{TT}N_T(t)]$$

(We suppose that we have no absorbing species at 347 nm except the triplet state, by assuming the same behaviour as in valerophenone.) The optical
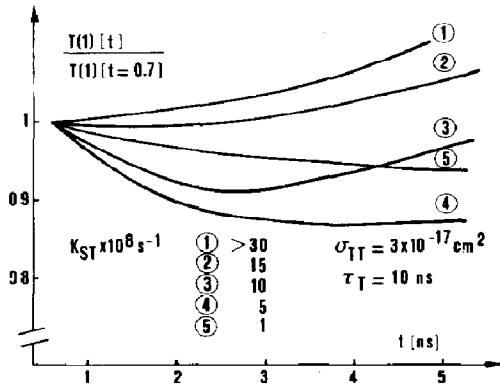
Fig. 5. Calculated transmission as a function of the optical delay t for different values of K_{ST}.

delay may be changed since the mirror (M) is movable along the laser beam axis. It is therefore possible to record a table of mn calculated values of the transmission in order to compare with the experimental data (m being the number of pulses in the train and n the number of experiments, each one with a particular optical delay t). These computer calculations are undertaken assuming that K_{ST}, τ_T and σ_{TT} are parameters. However, it is necessary to diminish the field in which these three parameters are allowed to vary. For this purpose, previous calculations showed that the general behaviour of the transmission between any two consecutive pumping pulses may be related to the intersystem crossing rate constant as follows (Fig. 5). $K_{ST} > 3 \times 10^9$ s^{-1}: the transmission continually increases, $K_{ST} \sim 10^9$ s^{-1}: the transmission decreases swiftly, then increases, $K_{ST} \sim 10^8$ s^{-1}: the transmission continually decreases.

In the same way, by making some assumption concerning τ_T or σ_{TT}, it is also possible to correlate some other experimental behaviour with these parameters. With regard to σ_{TT}, a good estimation of its values can be obtained by observing that the first pulse of the interrogating beam carries out the transmission of the sample not yet affected by the process of building up. Hence, computation and comparison with the experimental data becomes possible. The determination of the three parameters K_{ST}, σ_{TT}, τ_T is achieved as follows. First, the intersystem crossing rate constant, K_{ST}, is estimated from the shape of the transmission between two pulses, then, for a particular optical delay, the triplet absorption cross-section is deduced from the curve $T(1) = f(\sigma_{TT})$ (Fig. 6), and finally the lifetime τ_T is drawn from the computer family of curves showing up the variation of $T(4)/T(1)$ vs. τ_T with σ_{TT} as a parameter and for a given value of K_{ST} (Fig. 7).

By way of illustration, let us apply this processing to the case of PVPK in trichloromethylbenzene. The experimental results are displayed in Table 1 with mn values of the transmission (m and n having the same meaning as in the aforementioned case of computed results). The observed shape of the transmission between the first and the second pulses of the train leads us to
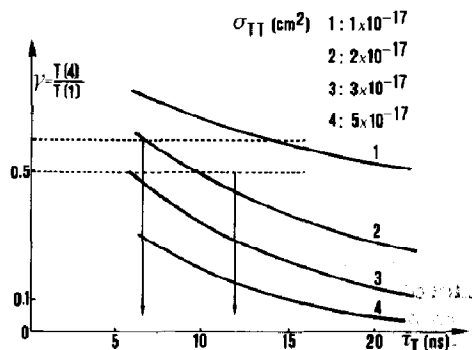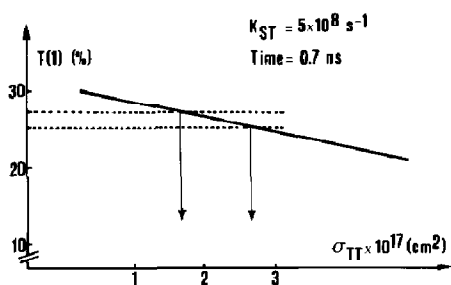
Fig. 6. Calculated transmission $T(1)$ of the solution on the pulse number one as a function of the triplet cross-section, σ_{TT}.

Fig. 7. γ ratio between the transmitted pulses number four and number one vs. the triplet lifetime, τ_T, as a function of the triplet cross-section, σ_{TT}.

TABLE 1

Experimental transmission (%) for PVPK in trichloromethylbenzene

Optical delay (ns)	Pulse number			
	1	2	3	4
0.7	26.2	20.8	16.5	15
2	22.8	19.4	18.1	16.9
3.3	21.6	18.7	17.1	17.6
5.3	19.4	15.8	14.3	14.2

an estimation of K_{ST} of about $1 - 5 \times 10^8$ s^{-1}. The experimental value $T(1)$ corresponding to $K_{ST} = 5 \times 10^8$ s^{-1} and the optical delay $L = 0.66$ ns is 0.27 from which we can deduce $\sigma_{TT} = 1.5 - 2.5 \times 10^{-17}$ cm^2. Thus, the ratio γ ($\gamma = T(4)/T(1)$) corresponding to the same optical delay drawn in the adapted family of curves $\gamma = f(\tau_T)$ leads to the value $\tau_T = 9 \pm 3$ ns. Changing the optical delay and using the experimental results related to the other pulses of the train, shows that the results are in the limits of experimental errors. Results of the same order are obtained by taking $K_{ST} = 10^8$ s^{-1}.

The following results have been obtained: $\tau_T = 9 \pm 3$ ns; $K_{ST} = 1 - 5 \times 10^8$ s^{-1}; $\sigma_{TT} = (2 \pm 1) \times 10^{-17}$ cm^2. The approximate value of σ_{TT} itself may be accounted for by the lack of precision in the energy determination of the excitation beam, but this has only a slight perturbating effect on the other parameters. This method has been applied to the study of the solvent dependence of the triplet lifetime and the rate constant of the intersystem crossing of PVPK. Table 2 summarizes the results.

The τ_T values are in good agreement within a factor of two with those previously deduced by Wagner [2] in Stern–Volmer experiments for valero-

TABLE 2

Intersystem crossing constant and triplet lifetime of PVPK in various solvents

Solvent	$K_{ST} \times 10^{-9}$ (s^{-1})	$\tau_T \times 10^9$ (s)
benzene	>3	7 ± 2
chlorobenzene	>3	7 ± 2
o-dichlorobenzene	1 - 3	8 ± 3
s-trichlorobenzene	0.5 - 1	8 ± 3
trichloromethylbenzene	0.1 - 0.5	9 ± 3

phenone and PVPK in benzene. Triplet lifetimes are not likely to be influenced by the kind of solvent. The quantum yield of triplet generation and consequently the six membered ring formation are highly dependent on the solvent viscosity.

Conclusion

We have shown that picosecond spectroscopy is also a versatile technique for studying transients in the nanosecond time scale and have obtained, for the first time, a direct measurement of the carbonyl triplet lifetime in a polymer. The triplet state is presumably the primary generation process in the Norrish type II photodegradation and the laser photolysis technique would be of interest to investigate the biradical generation, which is assumed to arise in a more protracted span of time scale.

Just after this work had been done, we become acquainted with a paper by Schnabel *et al.* [15] in which they emphasized the fact that the triplet state of PVPK has a lifetime in the order of 100 ns, as determined by laser spectroscopy. At present, we are not able to account for the discrepancy with our results; we may suppose that the transient observed in the long time scale arises from the excited singlet state *via* the intermediate state we have substantiated. In a forthcoming paper, we intend to present evidence for this hypothesis.

Acknowledgements

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