Triplet State of *O*-Acyloximes Studied by Time-Resolved Absorption Spectroscopy

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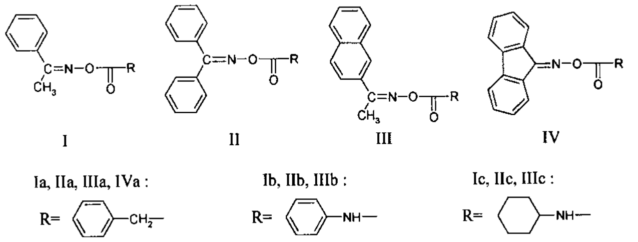
Triplet states of *O*-acyloximes were studied for the first time by means of laser absorption spectroscopy. Energy transfer experiments showed that the acyl moiety has no effect on the triplet energy, which depends only on the ketone oxime part. It was observed that the difference between the triplet energy of the parent ketone and that of the oxime varies, depending on the oxime structure. This behaviour is explained on the basis of a non-vertical character of the energy transfer reaction.

Photogenerating reactive species is a challenge for the development of new polymeric photosensitive systems. While most of the systems deal with photoinitiators generating radicals under light irradiation, photoacids and photobases have known a growing interest these last years.[1] Recently *O*-acyloximes have been reported as efficient photobase generators, and their use in photoresist cross-linking has been demonstrated.[2–4] It is known that excited *O*-acyloximes undergo a homolytic cleavage leading to iminyl and acyloxyl radicals.[5,6] This mechanism takes place from the triplet state of the oxime derivative, and therefore, the triplet energy level is the key factor in the photodissociation or in further photosensitization process. However, no values obtained by direct measurement are available in the literature. In this paper, we will determine by time-resolved laser spectroscopy the triplet energies of different *O*-acyloximes which differ both by the structure of the acyl moiety and by the ketone oxime one.

Different *O*-acyloximes were synthesized (Scheme 1) by a procedure described elsewhere.[7]



Scheme 1.

The nanosecond transient absorption setup is based on a pulsed solid state tunable laser (Nd:Yag laser operating at 10 Hz that delivers nanosecond pulses at 355 nm with an energy about 500 mJ). The laser pumped optical parametric oscillator

Table 1. Quenching rate constant of triplet donors by the various O-acyloximes

Energy donor	E_T^{D} [a] /kJ mol^{-1}	Ia	Ib	Ic	IIa	IIb	IIc	IIIa	IIIb	IIIc	IV
		log k_q									
Xanthone	310	9.7	9.7	9.7	9.7	9.7	9.7	9.72	9.9	9.77	9.84
Benzophenone	287	9.2	9.2	9.3	9.23	9.2	9.3	9.72	9.9	9.77	9.8
Phenanthrene	260	8.4	8.7	8.7	8.41	9	8.84	-	-	-	-
4-Phenylbenzophenone	255	8	8.31	8.34	8.3	8.6	8.48	9.59	-	-	-
9-Cyanophenanthrene	243[b]	6.6	7.2	7.8	-	7.84	7.7	-	-	-	-
Chrysene	238	7.14	6.8	7.6	6.7	7.3	7.3	9.2	9.53	9.47	9.75
Fluorenone	223[b]	5.95	-	-	-	-	-	-	-	-	9
Benzil	223	6	-	5.84	4.9	-	-	7.7	7.86	7.97	8.45
Pyrene	203	-	-	-	-	-	-	6.41	6.3	6.3	-
		E_T^{O} /kJ mol^{-1}									
		250	258	250	255	255	257	229	230	228	228
		E_T^{K}-E_T^{O} /kJ mol^{-1}									
		60	52	60	32	32	30	19	18	20	5
		Slope /mol kJ^{-1}									
		0.062	0.088	0.072	0.097	0.074	0.069	0.083	0.097	0.092	~0.2

[a] From Ref. 9 unless indicated. [b] From Ref. 12.

generates narrowband radiation in the visible and near-infrared spectral region that can be also frequency doubled. The wavelength is tunable continuously from 225 nm up to 1800 nm with an energy about 50 mJ at 550 nm.

Direct excitation of *O*-acyloximes does not reveal any absorbing transient that can be ascribed to triplet state. However the triplet state of the molecule can be studied by sensitization. Indeed, the lifetime of the donor triplet state is decreased by interaction with an acceptor compound, and the rate constant of interaction k_q can be determined by using the Stern–Volmer analysis. The results concerning the quenching experiments of triplet donors (in degassed benzene solutions) with well-defined energy levels E_T^D are collected in Table 1. It can be seen that for high E_T^D values, k_q is nearly diffusion-controlled. When E_T^D decreases, the reaction becomes more endergonic and k_q decreases. This fact is consistent with an energy transfer mechanism from the donor to the *O*-acyloxime.[5] From the plot of k_q vs E_T^D, an estimate of the energy level of the oxime excited state can be deduced according to the Sandros relationship[8]:

$$k_q = \frac{k_{exo}}{1 + \exp\left(\frac{-\Delta E}{RT}\right)} \qquad (1)$$

where k_{exo} is the rate constant for exothermic reaction and $\Delta E = E_T^D - E_T^O$ the difference between the donor triplet energy E_T^D and that for the acyloxime E_T^O (k_{exo} was taken equal to the k_q value measured for xanthone as a sensitizer). The value of E_T^O was iteratively adjusted to obtain the best fits between calculated and experimental curves.

From the results collected in Table 1, it is found that the nature of the acyl moiety (in the a, b, c series) does not affect by more than 10 kJ/mol the energy level of the ketone oxime triplet state: this has been already mentioned on the basis of steady state photolysis experiments on a series of ketone oxime compounds.[5] It follows that the triplet character is localized on the ketone oxime part of the molecule. This fact is supported by the values of the triplet energies which decrease with increasing the delocalization, a behaviour similar to that observed for the parent ketones. On the basis of a small set of steady-state phosphorescence quenching experiments, it has been supposed previously[5,6] that the energy level of the acyloxime triplet state E_T^O was close to the parent ketone one E_T^K. In the case of the compounds studied here, this statement is only valid for the acetonaphtone (III) and fluorenone (IV) oximes, and the difference $E_T^K - E_T^O$ lies within 20 kJ/mol (acetonaphtone:[6] E_T^K = 248 kJ/mol; fluorenone:[9] E_T^K = 223 kJ/mol).

Interestingly, in the case of type I and II compounds the triplet energies strongly differ in comparison to acetophenone (310 kJ/mol)[9] and benzophenone (287 kJ/mol)[9], respectively, and the difference $E_T^K - E_T^O$ varies from ca. 30 kJ/mol for the latter to more than 50 kJ/mol for the former. As a consequence, no general rule can be drawn to estimate the energy level of the oxime triplet state from that of the corresponding ketone.

A second interesting feature turns out from the plot of the quenching rate constant vs the triplet energy (Figure 1). In the endergonic or moderately exergonic region, the experimental points can exhibit a slope lower than that calculated from eq 1, i.e., 0.17 mol/kJ (Table 1). This departure from the Sandros behaviour is generally ascribed to a change in the geometry of the molecule between the ground and the excited states, and is referred to non-vertical energy transfer.[10–12] This effect is particularly important when the geometry change affects the orbital involved in the transition, and results in a lower value of the triplet energy than derived from eq 1.[13] It also explains the change in energy level between solution and glassy matrix (305 kJ mol^{-1} for IIa at 77K[6]). Such a behavior has been observed for stilbene or styrene derivatives, and the involvement of the formal carbon–carbon single bond torsion has been clearly evidenced.[11–13] Indeed in the present cases, a glance at Table 1 shows that greater is the $E_T^K - E_T^O$ difference, lower is the value of the slope, i.e., greater is the non-vertical behavior. Concomitantly, this trend corresponds to an increase in the flexibility of the molecule: fluorenone oxime is essentially planar, whereas acetophenone has a freely rotating phenyl ring. This particular behaviour will be examined on an appropriate series of derivatives and discussed in more details in a forthcoming paper.

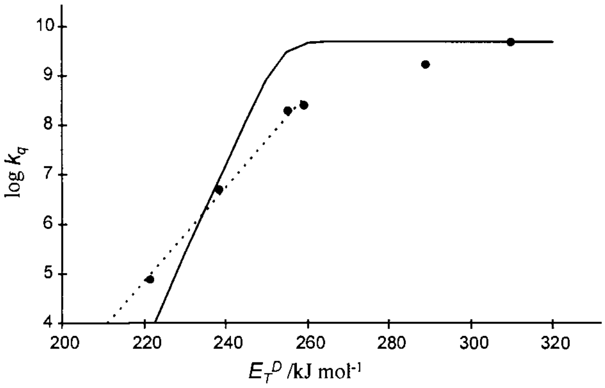


Figure 1. Plot of the quenching rate constant k_q vs the donor triplet energy E_T^D for compound IIa (•); theoretical curve predicted by Eqn.1 (——); linear analysis giving the slope of the curve in the endergonic region (-----).

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