Photocleavage Processes in an Iminosulfonate Derivative Usable as Photoacid in Resist Technology

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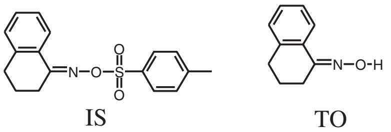
The cleavage process of an iminosulfonate was studied through time resolved laser spectroscopy. The S_0-S_1 and S_0-T_1 transitions were located on the oxime moiety. Under excitation, the cleavage process occured through a singlet mechanism. Under sensitized excitation, an efficient cleavage of the N–O bond occured in the triplet state of the iminosulfonate. The photoreactivity of this compound was compared to that of parent photobase generators (the *O*-acyloximes) based on the same oxime chromophore.

In photoresist technologies, the term "photoacid generator" is applied on compounds leading to the formation of acids under light exposure. Among them, non-ionic photoacids have received a particular attention,[1–4] due to their better solubility in solvents and polymer films than that of ionic photoacids (such as onium salts). Iminosulfonates are typical representatives of photoacids : the formation of sulfonic acid as well as their efficiency in photocrosslinking reactions have been clearly demonstrated.[5,6] However, despite their use under direct excitation, nothing is known concerning their cleavage mechanism.

Following our works on some acyloximes,[7,8] usable as photobases, the present paper is devoted to the investigation of the cleavage process in the particular iminosulfonate (IS) shown in Scheme 1, and based on the same oxime chromophore.[1,7,8] For comparison, the parent compound tetralone-oxime (TO) was used as a model. The properties of photoacids or photobases can obviously be ascribed to the *O*-substituents used. Indeed, sulfonate and some acyl moieties lead to the formation in the medium of sulfonic acid and amine, respectively.

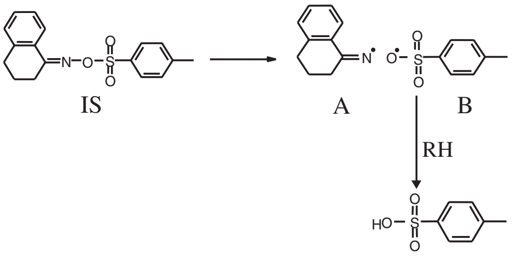


Scheme 1.

The overall mechanism of sulfonic acid generation in IS is shown in Scheme 2.[2]

UV–visible absorption spectra of IS and TO, shown in Figure 1, are very similar, demonstrating that the S_0-S_1 transition of IS is localized on the oxime moiety. This behaviour is similar to that of acyloxime derivatives.[8]

The time resolved laser spectroscopy apparatus is based on an optical parametric oscillator (Sunlite, Continuum) pumped by a Nd/YAG laser, together with a classical analysis device (LP900 Edinburg Instruments). This experimental setup has been fully described elsewhere.[8]



Scheme 2.

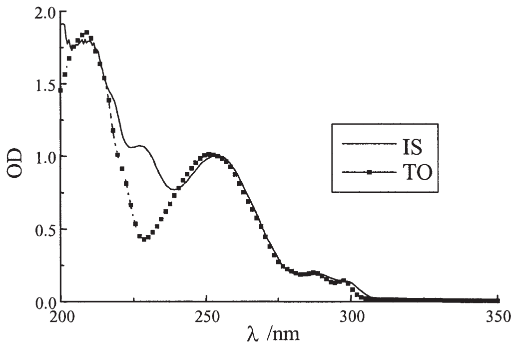


Figure 1. UV–visible absorption spectra of IS and TO in acetonitrile.

Direct laser excitation of IS and TO at 270 nm in acetonitrile did not lead to any detectable triplet state. On the other hand, a long-lived transient (no decrease in the absorption within 50 μs) was recorded for IS, the kinetics of which being not affected by the presence of oxygen. This transient can be ascribed to the iminyl radical (A in Scheme 2) already observed during the photolysis of acyloxime compounds,[8,9] a result that clearly supports the dissociation mechanism proposed in Scheme 2. Sulfonyloxyl radicals (B in Scheme 2) have been already observed in acetonitrile.[10] In our experimental conditions, likely due to the overlap with iminyl radical absorption, no significant absorption ascribable to sulfonyloxyl radical was detected, preventing to follow the generation of acid.

The triplet states of IS and TO were investigated through energy transfer experiments in a similar way to that already reported for oximes and with the same energy donors.[7,8,11,12] The evolution of the bimolecular quenching rate constant k_q for the energy transfer reaction between various triplet energy donors and IS or TO is shown in Figure 2. The Agmon-Levine-Balzani treatment, already used in our previous works on oximes,[7,11,12] was applied to fit the experimental data obtained. This leads to the values of 253 and 238 kJ/mol for the triplet energies of IS and TO,

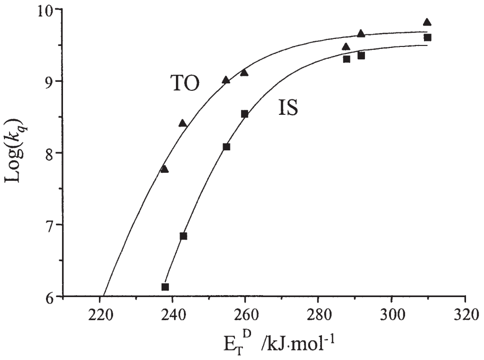


Figure 2. Quenching plots for the energy transfer experiments in benzene for compounds IS and TO : Log(k_q) vs the triplet energy of the donors.[12]

respectively. It clearly ensues that the sulfonate moiety slightly affects the triplet energy level of the molecule. Moreover, the slopes of the curves in the endothermic region are very similar, suggesting a non-vertical character for the energy transfer process that is typical when a torsion of the molecule occurs with the transition (as shown for other flexible oximes)[12] and confirms the localization of the S_0-T_1 transition on the oxime moiety for IS.

In these energy transfer experiments, the triplet state of IS or TO was not detected which presumes a short lifetime for these states. On the other hand, under this sensitized excitation of IS, the same long-lived transient state (corresponding to the iminyl radical) as the one obtained under direct excitation was observed (Figure 3). This experiment clearly supports a cleavage of the N–O bond in the triplet state.

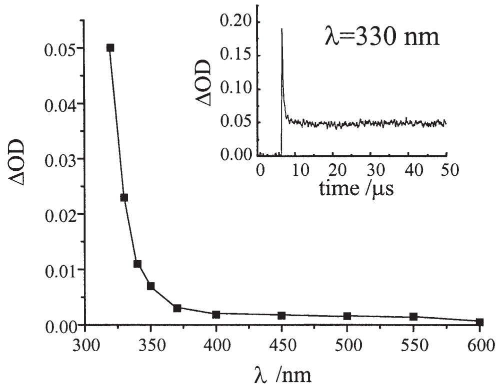


Figure 3. Transient absorption spectrum of the iminyl radical in benzene (recorded 4 μs after excitation at 355 nm) obtained under excitation of IS in the presence of benzophenone. Insert: long-lived iminyl radical absorption observed at 330 nm.

Evaluation of the amount of iminyl radicals formed was done, first under direct excitation of IS at 270 nm and then under sensitized excitation using benzophenone as the energy donor at 355 nm, with the same luminous energy absorbed for these two experiments. The yield in iminyl radicals under direct excitation was found very similar (although 10% higher) to that obtained under the sensitized excitation in acetonitrile. Assuming, on the basis of the acyloximes studies, that the triplet quantum yield is low, this experiment means that the cleavage process under direct excitation results probably from a fast reaction in the singlet state.

In conclusion, iminosulfonate photoacids exhibit a close analogy with acyloxime photobases concerning their photoreactivity. Both families exhibit S_0-S_1 and S_0-T_1 transitions localized on the oxime moiety of the molecule and, as a consequence, a very slight influence of the acyl or sulfonate substitution on absorption properties can be observed. An efficient dissociation occurs in triplet state. In addition, the photoacid studied exhibits a fast singlet state cleavage ability that explains its high efficiency under direct excitation and its application in the field of polymer technology.

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