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Introduction

Cyclohexanedione oxime herbicides are a class of compounds which show an excellent herbicidal activity against various weed species.¹ Moreover, some maize varieties are tolerant to this class of herbicides. This tolerance increases their potential interest as herbicides and justifies studies aiming at a better understanding of their fate in the environment. The chemical structures of some of the main herbicides of this family are given in Scheme 1. These species bear two keto groups that can undergo enolization and an *O*-substituted oxime which may be represented by either one of the isomers *E* and *Z*. The *E* form is more active as a herbicide, and cyclohexanedione oximes are therefore marketed in this isomeric form.

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Photolysis of cycloxydim, a cyclohexanedione oxime herbicide. Detection, characterization and reactivity of the iminyl radical

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Cyclohexanedione oxime herbicides have been reported to be readily photodegraded in the environment but the reaction mechanism has never been studied in detail. Here we investigated the photolysis of cycloxydim (CD) in acetonitrile and water, solvents in which CD is present as two distinct tautomeric forms: keto form in water and enol form with an intramolecular hydrogen bond between the enolic proton and the nitrogen atom of the oxime in acetonitrile O–H…N. CD (*E* isomer) undergoes photoisomerization in water but not in acetonitrile. This difference is attributed to the inhibiting effect of the intramolecular hydrogen bond existing in acetonitrile. In both solvents, irradiation of CD leads to the cleavage of the N–O bond as evidenced by the imine formation. The iminyl radical could be detected in acetonitrile by nanosecond laser-flash photolysis ($\lambda_{max} = 280$, 320 and 480 nm, $\tau \sim 100 \, \mu$ s). This radical is unreactive toward oxygen but readily abstracts an H atom from methanol ($k = 1.8 \times 10^5 \, \text{M}^{-1} \, \text{s}^{-1}$). Quantum calculations confirm the assignment of the transient species to the iminyl radical by showing that (i) the most stable structure of the iminyl carries a large spin density on the ring carbon and on the nitrogen atoms, (ii) the enolic H atom is transferred to the nitrogen atom and (iii) the intramolecular hydrogen bond O···H–N is responsible for both the iminyl long wavelength absorption and its high hydrogen abstraction reactivity.

> Cyclohexanedione oxime herbicides are reactive molecules not only under irradiation but also in the dark in acidic medium.¹⁻⁹ Scheme 2 summarizes the main reactions observed in the dark and under light exposure: isomerization of the oxime, oxazole and imine formations. Isomerization of the E-isomer into the Z-isomer has been reported in water, in the dark and under irradiation.^{2,5} The dark reaction, on the one hand, is made possible by the acidic hydrolysis of the oxime which allows the rotation of the O-alkyl about the C-N bond.¹ The photochemical isomerization of oximes, on the other hand, is well-known and studied for a long time.¹⁰ The formation of oxazole from cyclohexanedione oxime herbicides has also been reported.⁴ In the dark, this reaction occurs via N protonation followed by cleavage of the N-O bond, loss of R₃OH, Beckmann type rearrangement and final cyclization. Oxazole can also be produced photochemically, the reaction being observed in various media such as water, methanol and soil surface. Lastly, the imine is the main photoproduct in solid and in solution. Its formation is very minor in the dark.

> The oxime function is clearly at the core of the (photo)reactivity of these compounds. Thus, this is important for explaining why photoisomerization of cyclohexanedione oxime

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Scheme 2 The main photochemical and dark reactions of cyclohexanedione oximes reported in the literature.

herbicides occurs only in water or protic solvents. In this work, this point is addressed by looking at the relationship between solvent interactions and molecular configuration, with particular emphasis on the keto–enol tautomerism.

Another interesting issue is the nature of the intermediate species involved in the imine formation. The photocleavage of the N–O bond is a well-known reaction and yields the iminyl and alkoxy radicals.¹¹ EPR was successfully used in the literature to characterize iminyl radicals. To our knowledge, this radical was rarely observed by laser flash photolysis.

Our goal was to understand the photolysis mechanism of these compounds, in particular to explain the absence of photoisomerization in aprotic solvents and characterize the intermediate species involved in the imine formation. Experiments conducted on cycloxydim were rarely carried out in acetonitrile and neutral water. In addition to the steady-state irradiation that was used to measure the quantum yields of photolysis and characterize the main photoproducts, we investigated the reaction by means of nanosecond laser flash photolysis. The mechanisms were supported by quantum calculations.

Experimental part

Chemicals

Cycloxydim (98.1%) was obtained from Fluka and used as received. Acetonitrile was purchased from Prolabo (Hypersolv Chromanorm, 99.9% purity) and methanol from Sigma Aldrich (Chromasolv, 99.9% purity). The ultra-pure water used was from a Millipore Milli-Q system.

Irradiation

Steady-state irradiation at 334 nm was conducted in a device equipped with a high pressure Hg lamp (200 W) and a Bausch and Lomb monochromator. For irradiation at 278 nm, we used a high pressure xenon lamp (1600 W) equipped with a Bausch and Lomb monochromator. Photon fluence rates were measured using an Ocean Optics radiometer. These rates were 3.9×10^{14} photons cm⁻² s⁻¹ at 334 nm and 3.8×10^{13} photons cm⁻² s⁻¹ at 278 nm. Laser flash photolysis was carried out using a nanosecond laser-flash photolysis spectrometer from Applied Photophysics (LKS.60) with laser excitation at 266 nm from a Quanta-Ray GCR130-1 Nd:YAG laser. Experimental details are described elsewhere.¹² Solutions were deoxygenated or suroxygenated directly in the cell under argon or oxygen flow, respectively. The laser pulse energy (P) was measured using a joulemeter from Ophir Optronics Ltd. The absorbance at the pulse end (A) was measured for various P values to check the linearity of the dependence of A on P. In this case, the slope A/P is proportional to the $\varepsilon \times \Phi$ product of the transient where ε is the molar absorption coefficient and Φ the quantum yield of formation of the transient. Benzophenone was used as a chemical actinometer and photolyzed at the same absorbance at 266 nm as CD. The formation of the benzophenone triplet excited state was monitored at 520 nm $(\varepsilon_{\rm T} \times \Phi_{\rm T} = 6500 \text{ M}^{-1} \text{ cm}^{-1})$.¹³ The $\varepsilon \times \Phi$ product of the CD transient was obtained using the relationship: $\varepsilon \times \Phi = 6500 \times (A/P)$ - $(A/P)_{BP}^{-1}$. EPR experiments were conducted using a Bruker EMX EPR spectrometer interfaced with a computer equipped with WinEPR Acquisition System software. CD solutions were irradiated using a 1000 W Xe-Hg arc lamp (Schoeffel Instruments).

Analyses

UV-visible spectra were recorded using a Cary 3 (Varian) spectrophotometer.

The HPLC analyses were performed using a Waters apparatus equipped with a pump model 515 and a detector model 996. The column was a KinetexTM C18, 100 mm × 2.1 mm, with a particle size of 2.6 μ m, and a size pore of 100 Å. The eluent was a water–acetonitrile mixture. The mixture was kept at 50:50 (v/v) for 3 min and then the percentage of acetonitrile was increased linearly to reach 80% at 6 min. The flow was set at 0.2 cm³ min⁻¹. Mass spectrometry was performed using an LC/QTOF apparatus equipped with an orthogonal geometry Z-spray ion source (Waters/Micromass, Manchester, UK). Analyses were performed in positive mode. UV detection under MS heading was done using a Waters Alliance 2695 photodiode array detector system. The same conditions (column, gradient and flow) as those described above were used.

The NMR spectroscopy analyses of CD were performed in CD_3CN and D_2O and recorded using a Brüker 400 MHz (101 MHz for ¹³C) spectrometer using TMS as an internal standard. The following data were obtained:

¹H NMR (400 MHz, CH₃CN) δ 15.04 (s, 1H), 4.11 (q, J = 7.0 Hz, 2H), 2.85 (dd, J = 7.7 Hz, 2H), 2.58 (td, J = 11.4, 3.0 Hz, 2H), 2.54–2.42 (m, 2H), 2.38–2.25 (m, 2H), 2.10–1.99 (m, 2H), 1.85 (m, 1H), 1.71–1.7 (m, 2H), 1.52 (sext, J = 7.8 Hz, 2H), 1.28 (t, J = 7.0 Hz, 3H), 1.21 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H).

 $^{13}\mathrm{C}$ NMR (101 MHz, CD₃CN) δ 195.6, 185.6, 163.7, 107.1, 69.6, 41.3, 36.3, 30.3, 28.7, 28.3, 27.8, 27.3, 19.6, 13.3, 13.20.

 13 C NMR (101 MHz, H₂O + D₂O + NaOH) δ 195.2, 195.1, 161.5, 111.0, 68.8, 41.2, 38.5, 37.9, 31.4, 30.6, 28.8, 27.9, 27.1, 18.3, 13.9, 13.8.

Quantum calculations

The theoretical calculations were performed with the Gaussian program¹⁴ at the DFT level with the hybrid B3LYP exchange and correlation functional and the 6-31G(d,p) basis set. Unrestricted Hamiltonians were used for the treatment of radical species. Geometries were fully optimized in the ground state and time dependent DFT (TD-DFT) calculations were performed at the B3LYP/6-31G(d,p) level to obtain the absorption spectra. The calculation of bond dissociation energies was also performed at the B3LYP/6-31G(d,p) level.

Results and discussion

Determination of the CD structure in acetonitrile and water

The absorption spectra of CD in acetonitrile and neutral water are given in Fig. 1. Significant differences are observed. In acetonitrile, the main absorption band is centered at 250 nm ($\varepsilon = 11\,200 \text{ M}^{-1} \text{ cm}^{-1}$) and a smaller one ($\varepsilon = 6800 \text{ M}^{-1} \text{ cm}^{-1}$) appears at ~280 nm. In water, the predominant band ($\varepsilon =$ 15600 M⁻¹ cm⁻¹) is centered at 282 nm. These spectral changes suggest that the solvent affects the keto–enol tautomerism and that acetonitrile and water stabilize two different



Fig. 1 UV-spectrum of CD in acetonitrile (dotted line) and in neutral water (full line).



Scheme 3 Keto-enol tautomeric structures of CD.

tautomeric forms. The keto-enol tautomeric structures of CD are shown in Scheme 3.

To delineate which form is predominant depending on the solvent, ¹H and ¹³C NMR spectra were recorded. Data obtained by ¹³C-NMR confirm that CD is in equilibrium between keto and enol forms and that this equilibrium depends on the solvent used for the NMR analysis. As shown in Fig. 2, in CD₃CN, carbons C₁ and C₃ are not equivalent, the chemical shift being 185.6 and 195.6 ppm. In D₂O, carbons C₁ and C₃ are equivalent and symmetric and give a quasi-identical chemical shift respectively at 195.1 and 195.2 ppm. We conclude that in D₂O, CD is in the keto form, C₁ and C₃ belonging to the carbonyls groups, while in CD₃CN, CD is in the enol form with C_1 and C_3 belonging to the enol and the carbonyl, respectively. Moreover, the ¹H-NMR spectroscopy analysis performed in CH₃CN reveals the presence of a signal at 14.14 ppm that is characteristic of the displacement of the enolic hydrogen atom (Fig. 3). This confirms the presence of an intramolecular hydrogen bond between the enol and the nitrogen of the oxime.

Steady-state photolysis

Under light exposure, CD (*E* isomer) disappears rapidly in acetonitrile or in water. Photolysis quantum yields, $\Phi_{\rm CD}$, were measured for a fixed concentration of CD (10⁻⁴ M) by monitoring the CD loss by HPLC. Irradiations were performed at 334 nm when acetonitrile was used as the solvent and at



Fig. 2 13 C-NMR spectra of CD in CD₃CN and D₂O.

278 nm when the reaction was investigated in water. In both cases, CD was irradiated in the absorption band extending above 295 nm, *i.e.* in the relevant one as far as environmental photolysis is concerned. Φ_{CD} are $(3.9 \pm 0.4) \times 10^{-2}$ for aerated and $(1.7 \pm 0.2) \times 10^{-2}$ for argon-purged acetonitrile and $(1.7 \pm 0.2) \times 10^{-2}$ $(0.3) \times 10^{-2}$ for aerated water. The latter value is higher than those reported in the market authorization application of the compound: 5.68×10^{-3} at pH 5, 1.87×10^{-4} at pH 7 and $2.02 \times$ 10⁻⁴ at pH 9 and obtained upon irradiation of CD with polychromatic light.¹⁵ From our data, the quantum yield of CD photolysis is significant in water and in acetonitrile (1.7×10^{-2}) and 3.9×10^{-2} in air-saturated medium). Adding to this the extending of the absorption band and the high extinction coefficients of CD until 315 nm in water and 330 nm in acetonitrile, one can expect a decay of CD under environmental conditions as is reported for the other cyclohexanedione oxime herbicides.¹

The main photoproducts were assigned by HPLC-MS in positive mode. Data are presented in Table 1. In water, four main photoproducts are detected along with CD (m/z = 326 in ES+, retention time = 10.2 min). Photoproduct I shows an m/z

value of 282 corresponding to the loss of 44 u (O–CH₂–CH₂) and is assigned to the imine. Photoproduct II has the same mass fingerprint as isomer *E*, but a retention time that is much shorter (3.3 *versus* 10.2 min). It is assigned to isomer *Z*. Photoproduct III gives an *m*/*z* value of 342 corresponding to the addition of 16 u (O) and is assigned to an oxidation product. Lastly, photoproduct IV shows an *m*/*z* value of 280 corresponding to the loss of 46 u (HO–CH₂–CH₃) and is consistent with the oxazole. These compounds are mentioned in the market authorization application.¹⁷ In acetonitrile, only the imine(i) and the oxidation product (III) are found.

Laser flash photolysis

The irradiation of aerated solutions of CD in acetonitrile gives at the end of the pulse the transient absorption spectrum shown in Fig. 4. This spectrum is very broad extending from 275 to 520 nm. The absorption maximum is located around 280 nm. Neither the formation nor the decay of this species is affected by argon-purging of the solution. The transient absorption decays slowly at 280, 350 and 500 nm with an apparent first order rate constant of 9000 s⁻¹ in air or in

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 Table 1
 Quantum yields of CD photolysis in various solvents and the main photoproducts

	Quantum yield		
Solvent (irradiation wavelength)	Aerated medium	Deoxygenated medium	Photoproducts in air saturated medium $(m/z \text{ in ES+, retention time, function})$
Water, neutral pH (278 nm)	$(1.7 \pm 0.3) \times 10^{-2}$		I (282, 3.0 min, imine) II (326, 3.3 min, isomer Z) III (342, 3.5 min, oxidation product)
Acetonitrile (334 nm)	$(3.9 \pm 0.4) \times 10^{-2}$	$(1.7 \pm 0.2) imes 10^{-2}$	IV (280, 4.6 min, oxazole) I (282, 3.0 min, imine) III (342, 3.5 min, oxidation product)

argon-saturated medium. Similarly, varying the CD concentration within the range 5×10^{-5} - 2×10^{-4} M does not change the decay rate. It can be concluded that a unique species is formed which does not react with oxygen or CD itself. We tried to trap this species using methanol as an H-donor molecule. The experiment was successful since the addition of methanol at levels between 10 and 66% (v/v) drastically increased the transient decay rate. Plotting the apparent first order decay rate constant against methanol concentration gives a linear relationship and a bimolecular rate constant of reaction of $1.8\,\times\,10^{5}~M^{-1}~s^{-1}$ (see the inset of Fig. 4). The intensity of absorbance at the pulse end increases linearly with the energy pulse demonstrating that the formation of this species is monophotonic. By actinometry, $\varepsilon \times \phi = 150 \pm 20$ and 30 ± 10 M^{-1} cm⁻¹ were obtained at 350 and 500 nm, respectively. Assuming $\phi = 1.7 \times 10^{-2}$, *i.e.* the value that was obtained by steady-state irradiation in argon-saturated medium, one deduces that the molar extinction coefficient of the transient species is equal to $8800 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$ at 350 nm and 1700 \pm 600 M⁻¹ cm⁻¹ at 500 nm. In water this transient species is also observed but the signal is too weak to be followed.

Quantum calculations

The formation of the imine indicates that the N–O bond is cleaved. Such a bond was shown to be broken with the formation of two radicals.¹⁶ Therefore, the theoretical calculations aimed first at identifying the most stable structure that was obtained upon the homolytic N–O bond breaking. Three structures (see Scheme 4) of doublet spin multiplicity were optimized in the ground state at the B3LYP/6-31G(d,p) level of theory.

While the non-resonant C species is clearly disfavored, it is found here that A is significantly more stable than structure B $(E_A - E_B = -10 \text{ kcal mol}^{-1})$ because the O…H intramolecular hydrogen bonding is strong in A $(R_{O...H} = 1.890 \text{ Å}, R_{N...H} =$ 1.028 Å). Note that B is twisted at the CCCN bond at this level of theory ($\delta' = -115.8^\circ$, see Scheme 4). Thus, B is expected to rearrange easily into A through CCOH internal rotation and hydrogen shift. The spin density (SD) analysis on structure A shows that the radical is mostly localized on the carbon atom that bridges the ring and the iminyl group: SD_{C(1)} = 0.63, SD_N = 0.41 (see Scheme 4 for labels). Note that the thianyl ring is

Fia. 3





Fig. 4 Transient species measured at the pulse end upon irradiation of CD (10^{-4} M) in acetonitrile. Absorbance at 266 nm = 0.5.

twisted in the optimized structure ($\delta_{CCCC} = -55.7^{\circ}$) (see Scheme 4 for labels).

The absorption spectrum of structure A was calculated by the TD-DFT method at the B3LYP/6-31G(d,p) level and is shown in Fig. 5. The characteristic absorption at 455 nm, the shoulder at 320 nm and the 240 nm absorption give strong evidence that the transient species observed experimentally (see Fig. 4) is the iminyl radical proposed in structure A. The absorption band observed experimentally between 450 nm and 550 nm is built upon the n/π^* ($\lambda_{\text{theo}} = 548$ nm) and π/π^* transitions ($\lambda_{\text{theo}} = 444$ nm). The strong O…H intramolecular hydrogen bond stabilizes the π^* orbital because the latter bears local bonding character on the O…HN atoms. This transition is thus shifted towards lower energies. The molecular orbitals involved in these transitions are shown in Fig. 6.

Mechanism

The photochemistry of CD is highly medium dependent. In acetonitrile, CD gives mainly two photoproducts: the imine and an oxidation product. In water there are two additional pathways: photoisomerization and oxazole formation. To rationalize the absence of photoisomerization in acetonitrile, it is necessary to consider the effect of the medium on the molecule structure. NMR and absorption data demonstrate that in a non-protic solvent such as acetonitrile, the enol form is stabilized by an intramolecular hydrogen bond with the oxime nitrogen. After the π/π^* oxime excitation, the C=N bond is weakened. This allows isomerization about the CN bond. However, here, the presence of the intramolecular bond is

Fig. 5 Absorption spectrum of the iminyl radical (structure A in Scheme 4) computed by the TD-DFT method at the B3LYP/6-31G(d,p) level.

expected to prevent such internal rotation and thus inhibits photoisomerization. The excited *E* isomer yields back the ground state isomer *E*. In contrast, in water, where the keto form is favoured due to intermolecular hydrogen bonds between the carbonyl and solvent OH, internal rotation is free and isomer *Z* can be obtained. The inhibiting effect of intramolecular hydrogen bonds on photoisomerization has been reported in the literature.^{17,18} Usually, photoisomerization is not found in non-polar solvents but observed in alcohol or acidic solvents because the latter are supposed to disrupt the intramolecular hydrogen bond.

The photochemistry of CD in acetonitrile involves the oxime. The N–O bond cleavage produces the iminyl and the alkoxy radicals. Quantum calculations show that the stable form of the iminyl radical has the electronic charge delocalized on the O–C–C–N atoms with the highest density on the nitrogen and carbon atoms. Moreover, the H-atom is borne on the nitrogen. This implies that a fast H-atom transfer from the enol to the nitrogen occurs after the N–O bond cleavage. Using these data, it can be deduced that the long-lived transient species observed in acetonitrile by laser flash photolysis is the iminyl radical. In accordance, this radical does not react with oxygen but is scavenged by methanol to yield the imine (Scheme 5).

Iminyl radicals have been intensively studied for synthesis purposes to generate new rings by intramolecular cyclisation. They can also abstract hydrogen atoms to yield imines: the rate constants for H-abstraction by iminyl radicals are reported to be more than an order of magnitude slower than that for



Scheme 4 Structures of the iminyl radical that were investigated in this work, $\delta = -55.7^{\circ}$ and $\delta' = -115.8^{\circ}$

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Fig. 6 The B3LYP/6-31G(d,p) π , n and π^* molecular orbitals involved in the 450–550 nm band of the absorption spectrum shown in Fig. 5.





C-centered analogues.¹⁹ For instance, the abstraction of a methanolic hydrogen (CH₃O–H) by methyl radicals at 300 K is $\sim 10^2 \text{ M}^{-1} \text{ s}^{-1}$.²⁰ Iminyl radicals should therefore be less reactive. Thus, the rate constant of the alcohol H-atom abstraction reaction between the radical obtained from CD and methanol seems rather high, indicating that this specific radical is more reactive than most of the iminyl species. Accordingly, attempts to detect the iminyl derived from CD by EPR were unsuccessful.

To explain such an unexpectedly high reactivity, dissociation energy calculations of the N–H bond (D_{N-H} in units of kcal mol⁻¹) were performed for three possible imine models (Scheme 6). In (a), the model species is representative of the iminyl radical investigated in this work: the key features of electron delocalization and the intramolecular hydrogen bond are accounted for in this structure. One gets $D_{N-H} = 98.4$ kcal mol⁻¹



Scheme 6 Theoretical N–H bond strengths of model molecules at the B3LYP/6-31G(d,p) level. D is purely electronic.

in this case. In (b), where one unit of unsaturation is removed, one finds that $D_{\rm N-H} = 104.2$ kcal mol⁻¹. Clearly, the electronic delocalization weakens the N–H bond. In (c) the carbonyl group was rotated to suppress the intramolecular hydrogen bond. Two different cases (c_a and c_b) were investigated. The most stable structure is that obtained in (c_b), where the singly occupied orbital is directed toward the methyl substituent. The respective N–H bond strength is $D_{\rm N-H} = 88.7$ kcal mol⁻¹. In this model, the corresponding radical iminyl no longer bears the intramolecular hydrogen bond. For the other structure (c_a) where the remaining H atom of the iminyl radical is directed toward the methyl group, $D_{\rm N-H} = 91.8$ kcal mol⁻¹. These calculations demonstrate the drastic reinforcing effect of the iminyl intramolecular hydrogen bond O····H–N on the strength of the second N–H bond.

Using these data, it is possible to estimate the effect of the intramolecular hydrogen bond on the iminyl H-abstraction ability. Let us consider the reaction

$$RN^{\bullet} + MeOH \rightarrow RNH + MeO^{\bullet}$$

The activation energies may be expressed as $E_a = \text{Cte} + \alpha \Delta H$, with $\Delta H = D_{\text{MeO-H}} - D_{\text{RN-H}}$.²¹ If RN-H and R'N-H represent the reactant molecules (a) and (c_b), respectively, the ratio of the rate constants k/k' is:

$$\frac{k}{k'} = \mathrm{e}^{\alpha(D_{\mathrm{RN-H}} - D_{\mathrm{R'N-H}})/RT}$$

 $D_{\text{RN-H}} - D_{\text{R'N-H}}$ is 9.7 kcal mol⁻¹. Taking $\alpha = 0.55$,²² one gets $k/k' = 8.1 \times 10^3$ at 298.15 K. Thus, the presence of the intramolecular hydrogen bond increases the abstraction rate constant by four orders of magnitude. These calculations confirm the experimental data.

The imine formation upon irradiation of CD in pure acetonitrile requires the abstraction of a mobile H atom. Some solvent impurities or CD itself might be the H-donor, but the concentration used here is low, making this reaction improbable. Alternatively, the H atom could be abstracted from the ethoxy radical that is produced along with the iminyl species through the N–O bond cleavage.

Along with the imine, an oxidation product (III) corresponding to CD + O is formed upon CD irradiation. Taking into account that the quantum yield of CD phototransformation is higher in the presence of oxygen than in its absence, it could be produced by oxidation of the CD excited state by oxygen. However, we did not observe the excited states by laser flash photolysis, in particular the triplet excited state. This absence may be due to several reasons: poor quantum yield of formation, poor absorption coefficient or a short lifetime. Another possibility for the formation of product III could be the oxidation of CD by radicals obtained in the N–O cleavage. However, this would not explain the quantum yield increase in the presence of oxygen.

To conclude, this study rationalizes the different results reported on cyclohexanedione oxime herbicides. For this class of compounds, the intramolecular hydrogen bond present in aprotic solvents governs a part of the photoreactivity. This feature explains the lack of photoisomerization under specific conditions. The intramolecular hydrogen bond in the iminyl radical also reinforces significantly the ability of this radical to abstract hydrogen atoms in comparison to other iminyl radicals. Under environmental conditions, in surface water or on a soil surface, the iminyl radicals generated from cyclohexanedione oximes would have many possibilities to react with natural compounds, either by H abstraction or by addition on double bonds. In this work, the iminyl radical was successfully detected in acetonitrile and its reactivity toward H-donor molecules measured.

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