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# Photochemical and sonochemical reactions of norharmane

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## Abstract

In this work, a study on the photochemical and sonochemical behaviour of norharmane in halomethane media (dichloromethane, chloroform, carbon tetrachloride and dibromomethane) is presented. When solutions of norharmane in these media are irradiated with UV light or sonicated with ultrasound at 20 or 50 kHz, the cationic species of norharmane appears in solution. In order to explain the formation of this species by a UV radiation effect, a exciplex (charge transfer complex) between norharmane and halomethane has been proposed. The formation rate constants of the exciplex were calculated using fluorescence quantum yields and lifetime values. The sonochemical formation of cationic species does not occur by formation of a charge transfer complex between norharmane and halomethane. In this paper, we report that an initially neutral medium can quickly develop acidity in a few minutes of exposure in a conventional bath to ultrasound.

*Keywords:* Norharmane; Photochemistry; Sonochemistry; Halomethane media

## 1. Introduction

Norharmane or $\beta$-carboline ($\beta$C) (Fig. 1) is markedly fluorescent alkaloid. The acid–base properties of $\beta$C and its derivatives have been largely studied in aqueous and ethanolic solutions [1–4]. In previous work [5], we have presented the photochemical–photophysical behaviour of norharmane in halomethane–acetic acid mixtures. In this medium, a new species with fluorescence maximum at 400 nm was detected. This fluorescence maximum only appears in the presence of dichloromethane– or chloroform–acetic acid mixtures. In carbon tetrachloride– or acetonitrile–acetic acid mixtures, this fluorescence was not observed. We associated this maximum with the formation of a hydrogen bond between the pyridinic nitrogen atom of norharmane and the hydrogen atom of halomethane.

Erra-Balsells and Frasca [6] studied the photochemical behaviour of $\beta$C in dichloromethane solution. They suggested a radical mechanism for these dimerization reactions and they propose that the formation of dimer products in dichloromethane solution would be by means the N–H bond photodissociation of the pyrrolic ring in two norharmane molecules. These researchers suggest that the photoreactive state nature is probably an n$\pi^*$ triplet. Biondic and Erra-Balsells also described the photochemical behaviour of $\beta$C in carbon tetrachloride–ethanol mixtures and chloroform [7,8]. In these media, the cationic species was only observed and the dimers were not detected. In the latter solvent, these workers propose a transient excited state between the excited singlet state of the norharmane and chloroform.

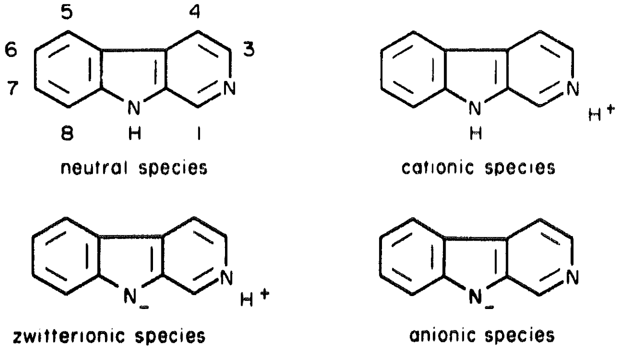

Fig. 1. Different forms of $\beta$C.

On the other hand and within our knowledgment, any study on the photochemical behavior of norharmane in dibromethane solutions has been reported.

Chae and Ham [9,10] report the photopolymerization of vinyl monomers initiated by $\beta$C in carbon tetrachloride solution as evidence for the photochemical radical formation of these compounds.

In this work, we have not observed formation of dimers in all solvents studied. We present a comparative study on the

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photochemical behaviour of $\beta$C in halomethane solutions: dichloromethane ($Cl_2CH_2$), chloroform ($Cl_3C$), carbon tetrachloride ($Cl_4C$) and dibromomethane ($BrCH_2$). In order to characterize this photochemistry, fluorescence quantum yields and lifetime values were obtained in these media.

In these solutions UV radiation and ultrasonication produce similar effects, the appearance of new absorption and fluorescence bands corresponding to the cationic species. This fact is important because the use of ultrasonic baths for a rapid solution of samples is a very extended practice in laboratories. We used this reaction to show that ultrasound can change the properties of media, so that a medium initially neutral can develop acidity in a few minutes of exposure in a conventional bath to ultrasound.

## 2. Experimental details

$\beta$C or norharmane from Sigma (base free, 98%) was used in our experiments. This alkaloid was of the best available quality and was used as received. The halomethane solvents used were Merck Uvasol grade.

The absorption spectra were obtained in a Cary-17 spectrophotometer. Fluorescence spectra were recorded in a Schoeffeld Instruments Corp. spectrofluorimeter with a 3 nm band width in excitation and 2 nm band width in emission. All experiments were carried out at 25.0 ± 0.1 °C. The solvents used exhibit negligible emission in the conditions of this work. Fluorescence spectra were not corrected.

The fluorescence lifetimes were obtained by the single-photon counting technique in an Applied Photophysics spectrometer using a pulsed nitrogen lamp. An exponential decay function was determined by non-linear least-squares iterative deconvolution. The goodness of fit was tested by noting the values of the weighted residuals, the plot of the autocorrelations function and the magnitudes of the reduced $\chi^2$ and Durbin–Watson (DW) parameter [11–14].

The fluorescence quantum yields of cationic species were determined by comparing the corrected emission spectra of $\beta$C in halomethane solution (2% ethanol + $H_2SO_4$) with the corrected spectrum of a standard solution of $\beta$C in aqueous solution of 0.1 N $H_2SO_4$ [15]. For the neutral species, the comparison is with the corrected emission spectrum of this species in ethanol. The fluorescence quantum yield values were calculated using the expression

$$\Phi_x = \Phi_s \frac{A_s(\lambda_s)}{A_x(\lambda_x)} \frac{I(\lambda_s)}{I(\lambda_x)} \frac{D_x}{D_s} \frac{n_x^2}{n_s^2}$$

where the subscripts s and x refer to the reference and the unknown solutions respectively, $\Phi$ is the quantum yield, $A(\lambda)$ is the absorbance per centimetre of solution at the excitation wavelength, $I(\lambda)$ is the relative intensity of the exciting light at the wavelength $\lambda$, $D$ is the integrated area under corrected emission spectrum and $n$ is the refractive index of the solution at the fluorescence maximum.

Generally, a conventional ultrasonic bath was used for ultrasound production (frequency, 50 kHz). In some cases, for quantitative studies, a 20 kHz frequency reactor with titanium horn (diameter, 2.5 cm) was used. Nuclear magnetic resonance (NMR) and mass spectra were obtained in a Bruker WH-200-Sy and Hewlett-Packard 5985 gas chromatography–mass spectrometry instruments respectively.

## 3. Results

### 3.1. *Sonochemistry of norharmane in halomethane media*

The absorption spectrum of $\beta$C in halomethane solution exhibits the characteristical profile corresponding to neutral species (two absorption maxima around 330 and 340 nm). When solutions are introduced into an ultrasonic bath, a new band appears in the 360–370 nm zone. In Fig. 2, the effects of ultrasound on the absorption spectrum of $\beta$C in $Cl_3CH$ are shown for different exposure times. This behaviour is general in all solvents used in this work. On the contrary, when these solutions are excited at 370 nm, the fluorescence spectrum presents a maximum around 445 nm in $Cl_2CH_2$, $Cl_3CH$ and $Br_2CH_2$. These fluorescence spectra are similar to the corresponding spectrum of the cationic species.

In carbon tetrachloride solution, the fluorescence spectrum of $\beta$C has a shoulder at 438 nm and a maximum at 501 nm. The fluorescence spectrum of $\beta$C in $Cl_4C$–$H_2SO_4$ solution also exhibits these two maxima (Fig. 3).

NMR spectra for different solutions were obtained to elucidate the nature of the species formed by ultrasonic irradiation. A stream of hydrogen chloride was bubbled into a $\beta$C solution in diethyl ether to form the cationic species. The sonospecies was obtained by sonication of $\beta$C in chloroform

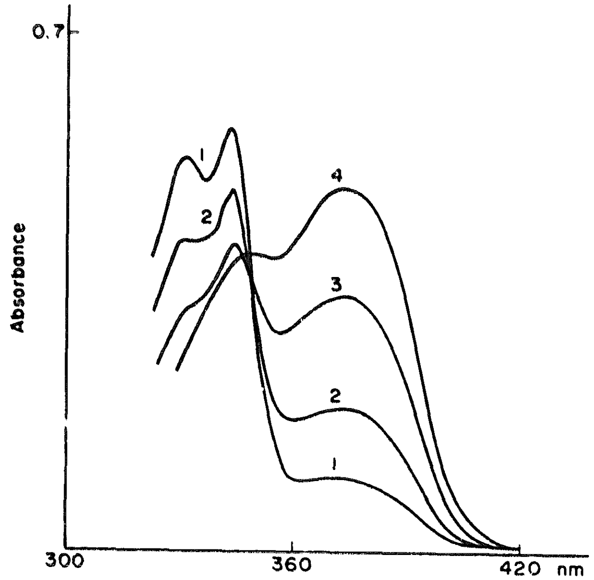

Fig. 2. Absorption spectra of $\beta$C in chloroform solution for different sonication times: spectrum 1, 10 min; spectrum 2, 20 min; spectrum 3, 30 min; spectrum 4, 60 min.

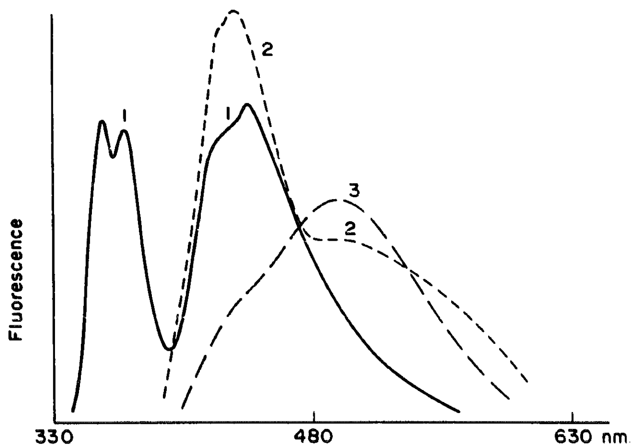

Fig. 3. Fluorescence spectra of norharmane in tetrachloride solutions: spectrum 1, $\lambda_{exc}$ = 337 nm; spectrum 2, solution with $H_2SO_4$ and $\lambda_{exc}$ = 380 nm; spectrum 3, sonicated solution and excitation, $\lambda_{exc}$ = 380 nm.

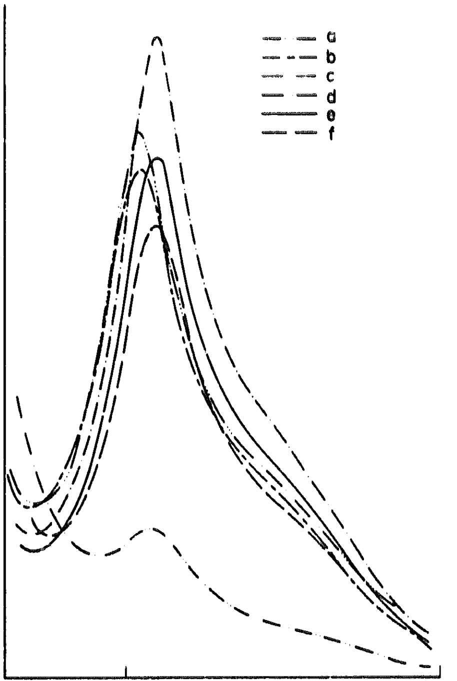

Fig. 4. Disappearance of DPPH in different sonicated (5 min) solutions: curve a, DPPH–methanol; curve b, DPPH–methanol with sonication; curve c, DPPH–chloroform; curve d, DPPH–chloroform with sonication; curve e, βC–DPPH–chloroform; curve f, βC–DPPH–chloroform with sonication.

solution and the solvent was removed subsequently by bubbling nitrogen into solution. Neutral, cationic and sono- species were dissolved in deuterated methanol and their NMR spectra were determined. The greatest shift if for the signals corresponding to hydrogen atoms on positions 1 and 3, 8.82 ppm and 8.31 ppm respectively for neutral βC vs. 9.18 ppm and 8.76 ppm respectively for the cationic βC obtained by treatment of βC with hydrogen chloride in diethyl ether. The same frequencies for H1 and H3 were observed for the sonospecies and thus we can assign the same cationic character for them. We also obtained the mass spectrum of the sonospecies and dimeric products were not observed.

Free radical formation can be measured quantitatively by scavenging the radicals with the stable purple free radical diphenylpicrylhydrazyl (DPPH) [16]. The disappearance of the scavenger can follow by measuring the decrease in optical density at 546 nm. We used DPPH to determine the possible presence of free radicals in the sonicated solution of βC in chloroform (Fig. 4). Three solutions were prepared and sonicated, DPPH in methanol, DPPH in chloroform and DPPH + βC in chloroform, with the following results.

(i) In pure methanol and pure chloroform, the sonication produces free radicals.

(ii) The production of free radicals is greater in chloroform than in methanol.

(iii) The rate of disappearance of DPPH in chloroform–βC solution is less than in pure chloroform.

### 3.2. *Photochemistry of norharmane in halomethane solutions: fluorescence lifetimes and quantum yields*

When a solution of βC in halomethane medium is irradiated where the neutral species absorbs (λ = 333 nm), a photoproduct is obtained. This product exhibits a fluorescence maxima around 453 nm in dichloromethane and dibromomethane solutions and 449 nm and 435 nm in chloroform and carbon tetrachloride respectively.

A study of fluorescence intensity variation with the irradiation time was made. We fixed the emission monochromator at 480 nm and we took fluorescence intensity values each minute. In these conditions, the representations of fluorescence intensity vs. exposure time are straight lines (Fig. 5). From this figure, the relative process rates for different solvents can also be obtained. The relative $k$ values are in the order

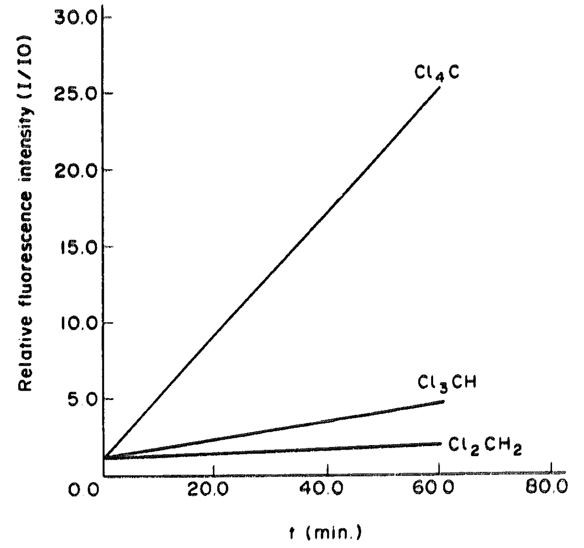

Fig. 5. Relative fluorescence intensity at 480 nm vs. time of irradiation at 337 nm.

Table 1
Fluorescence lifetimes and statistical parameters for different solutions of $\beta$-carboline

| Media | $\lambda_{exc}$, $\lambda_{em}$ (nm) | $\tau$ (ns) | $\chi^2$ | DW parameter |
|---|---|---|---|---|
| Dichloromethane | 337, 380 | 2.1 | 0.95 | 1.68 |
| Chloroform | 337, 380 | 2.1 | 1.02 | 2.11 |
| Carbon tetrachloride | 337, 380 | < 1 | | |
| Dibromethane | 337, 380 | < 1 | | |

$k(Cl_2CH_2) < k(Cl_3CH) < k(Cl_4C)$

The influence of norharmane concentration on the rate of photoprocess appears to be non-significant.

We also obtained the absorption and fluorescence maxima of cationic species in halomethane media by addition of $H_2SO_4$ traces to solution. Although sulphuric acid is not soluble in halomethane media, we have obtained a non-turbid solution of halomethane–$H_2SO_4$ by adding to 25 ml of halomethane small quantities of a slightly turbid halomethane–$H_2SO_4$ solution until we obtained the maximal concentration of acid for which the solution remained non-turbid. The absorption maxima in these solutions are around 370 nm–371 nm for $Cl_2CH_2$ and 373 nm for $Cl_3CH$ and $Cl_4C$ solutions. The fluorescence maxima are at 445 nm and 439 nm for $Cl_2CH_2$ and $Cl_3CH$ respectively and two maxima are found at 436 and 510 nm for $Cl_4C$ solution (see Fig. 3).

The fluorescence lifetime was measured for different solutions with the same $\beta$C concentration (Table 1). Halomethane media quench the fluorescence of neutral species. Thus, with excitation at 337 nm of a solution of $\beta$C in different ethanol–chloroform mixtures and gathering of the fluorescence at 380 nm, the fluorescence lifetime values varied from 4.3 ns, in pure ethanol, to 2.1 ns in pure chloroform. In pure dichloromethane this value is also 2.1 ns; in carbon tetrachloride and dibromomethane, the fluorescence lifetime values of neutral species are less than the limit of resolution of our instrumental device (below 1 ns).

We have measured the fluorescence quantum yields of neutral and cationic species in ethanol and in the four halomethane media studied in this work. The cationic species has the same value of this parameter in ethanol and chloromethane media ($\Phi_f = 0.6$). In dibromomethane solution, the fluorescence quantum yield of this species decreases strongly ($\Phi_f = 0.06$) (Table 2). In $Cl_4Cl$ solution with ethanol-$H_2SO_4$, the fluorescence spectrum of $\beta$C only exhibited a maximum around 442 nm.

$\Phi_f$ of neutral species do not remain constant in ethanol, chloromethane media and dibromomethane. The values measured are $\Phi_{Cl_2CH_2} = 0.69\Phi_{ethanol}$, $\Phi_{Cl_3CH} = 0.64\Phi_{ethanol}$, $\Phi_{Cl_4C} = 0.12\Phi_{ethanol}$ and $\Phi_{Br_2CH_2} = 0.04\Phi_{ethanol}$.

## 4. Discussion

The $\beta$C–halomethane system did not exhibit any significant interaction in the electronic ground state. In this medium, only the absorption of the neutral species is observed. In order to explain the formation of the cationic species by UV radiation an exciplex between $\beta$C and halomethane has been considered by several researchers [6–8]. Some theoretical publications [17–19] confirm this hypothesis. These publications reveal the tendency of some $\beta$C derivatives to form very stable charge transfer complexes with electronic acceptors in the $S_1$ state. Moreover, Pimentel and McClellan and Green [21] demonstrates the formation of donor–acceptor complexes between amines and halomethane through C--H--N hydrogen bonding. Therefore, taking into account these publications, we think that a donor–acceptor complex forms between the $\beta$C and halomethane molecule in $S_1$ state. This complex formation occurs through C--H--N hydrogen bonding. This interaction type is only possible in $Cl_2CH_2$, $Cl_3CH$ and $Br_2CH_2$ solvents but not in carbon tetrachloride. $Cl_4C$ is a solvent of high electron affinity and we consider the complex formation proposed by Erra-Balsells according with the following process:

$$[\beta C^{\delta+}\cdots CCl_4^{\delta-}] \longrightarrow [\beta C^{+\bullet}\cdots Cl^-\cdots {}^{\bullet}CCl_3] \longrightarrow$$
$$\beta C^{+\bullet} + Cl^- + {}^{\bullet}CCl_3$$

We think that these radicals can be stabilized by hydrogen abstraction from $H_2O$ traces present in $Cl_4C$ solution.

The observed reactivity in these media agrees with the results obtained for charge transfer complex formation between amines and halomethanes (Hal) [22,23] and with the following kinetic scheme:

$$\beta C + h\nu \xrightarrow{k_0} \beta C^*$$
$$\beta C^* \xrightarrow{k_f} \beta C + h\nu$$
$$\beta C^* \xrightarrow{k_d} \beta C + \Delta H$$
$$\beta C^* + \mathrm{Hal} \xrightarrow{k_1} \mathrm{Phsp}^*$$
$$\mathrm{Phsp}^* \xrightarrow{k_f} \mathrm{Phsp} + h\nu'$$
$$\mathrm{Phsp}^* \xrightarrow{k_\delta} \mathrm{Phsp} + \Delta H'$$

where Phsp indicates photospecies.

The above-mentioned interactions appear in the first electronic excited singlet state in the $\beta$C. In this state, this molecule undergoes a two-state excited state reaction which is irreversible. Thus, at 380 nm, only the neutral form emits, and therefore the experimental decay is monoexponential as

Table 2
Quantum yields for cationic and neutral species of $\beta$-carboline in different media

| Solvent | $\Phi_f$ (cationic species) | $\Phi_f$ (neutral species) |
|---|---|---|
| Ethanol | 0.6 | – |
| $Cl_2CH_2$ | 0.6 | $0.69\Phi_{ethanol}$ |
| $Cl_3CH$ | 0.6 | $0.64\Phi_{ethanol}$ |
| $Cl_4C$ | 0.6 | $0.12\Phi_{ethanol}$ |
| $Br_2CH_2$ | 0.06 | $0.04\Phi_{ethanol}$ |

is observed in Table 1. The fluorescence lifetime values agree with the $\Phi_f$ values of neutral species obtained in these media:

$$\tau_{Cl_2CH_2,n} = \tau_{Cl_3CH,n} > \tau_{Cl_4C,n} \text{ and } \tau_{Br_2CH_2,n}$$

$$\Phi_{Cl_2CH_2,n} \approx \Phi_{Cl_3CH,n} > \Phi_{Cl_4C,n} > \Phi_{Br_2CH_2,n}$$

Account is taken of the following expression for the fluorescence quantum yield of cationic species:

$$\Phi_{ethanol,c} = \Phi_{Cl_2CH_2,c} = \Phi_{Cl_3CH,c} = \Phi_{Cl_4C,c} = \frac{k_{f,c}}{k_{f,c} + k_{d,c}}$$

where $k_{f,c}$ and $k_{d,c}$ are respectively the radiative and non-radiative transition probabilities for the cationic species. From these results, we can consider that these probabilities have the same value in ethanol as in chloromethane media. In dibromomethane, a new non-radiative deactivation channel appears as a result of the heavy atom effect and $\Phi_f$ decreases strongly. For the neutral species, this parameter does not remain constant in ethanol and chloromethane media. For this species, a new deactivation channel appears which causes the photochemical reaction observed (cationic species do not exhibit photochemistry). If we compare the results for neutral and cationic species, we can also consider that, for the neutral species, $k_{f,n}$ and $k_{d,n}$ in ethanol have the same values as in chloromethane media. Thus, the following equations represent the fluorescence quantum yields for the neutral species in ethanol and chloromethane media:

$$\Phi_{ethanol} = \frac{k_{f,n}}{k_{f,n} + k_{d,n}}$$

$$\Phi_{chloro} = \frac{k_{f,n}}{k_{f,n} + k_{d,n} + k_{ln}}$$

where $k_{ln}$ is the transition probability obtained photochemically. Therefore, division of one of these equations by the other gives

$$\frac{\Phi_{ethanol}}{\Phi_{chloro}} = 1 + \frac{k_{ln}}{k_{f,n} + k_{d,n}}$$

and, because $\tau_{eth,n} = 1/(k_{f,n} + k_{d,n})$,

$$\frac{\Phi_{ethanol}}{\Phi_{chloro}} = 1 + k_{ln}\tau_{eth,n}$$

From this equation and with $\tau_{eth,n} = 4.3$ ns, the $k_l$ values in dichloromethane, chloroform and carbon tetrachloride are $1.0 \times 10^8$ s$^{-1}$, $1.3 \times 10^8$ s$^{-1}$ and $1.7 \times 10^9$ s$^{-1}$ respectively. In $Br_2CH_2$ solution, in addition to the photochemical deactivation, a non-radiative deactivation channel exists as a result of the heavy atom effect. For this solvent, we have not been able to measure the $k_l$ value.

With these values for $k_l$, we can not think as Erra-Balsells et al. did of a photoreactive state n$\pi^*$ triplet. Nevertheless, during the time of irradiation it is possible to populate triplet states and these states could cause the formation of βC dimers detected by these researchers in $Cl_2CH_2$ solution.

In carbon tetrachloride, we observed the formation of two photoproducts, the cationic form and another form which emits around 500 nm. Comparing with the results [1] in the literature, we associate the latter fluorescence with the emission of the zwitterionic form. In this solvent, the donor–acceptor complex formation between βC and $Cl_4C$ also occurs but in this case, without hydrogen bond formation. The $Cl_4C$ decomposition by light is more rapid in this solvent than in $Cl_2CH_2$, $Cl_3CH$ or $Br_2CH_2$, so that the $^{\bullet}Cl_3C$ concentration is very high in a few minutes. In the absence of ethanol or methanol, this radical can abstract hydrogen from the N–H pyrrolic group and the zwitterionic species can be formed. This fact would explain the fluorescence of the zwitterion observed for βC in $Cl_4C$–$H_2SO_4$ (without ethanol) solutions irradiated with UV light. The hydrogen donor character of primary alcohols in photochemical radical reactions is well known in the literature. Thus, in the presence of ethanol or methanol, the hydrogen abstraction of alcohol by $^{\bullet}Cl_3C$ radical occurs and only the fluorescence of the cationic species is observed.

The formation of βC hydrochloride by sonication does not occur via charge transfer complex formation. It is known in sonochemistry that the sonication of dichloromethane, chloroform and carbon tetrachloride in aqueous solution produces HCl [24–27]. In carbon tetrachloride the formation of HCl can be explained by traces of $H_2O$ present in solution. This behaviour agrees with the following experimental fact. If chloroform is sonicated for 5 min and βC is added after 10 min, formation of βC hydrochloride is observed. The HCl formed would be responsible for the formation of cationic species.

The presence of radicals in the βC–halomethane solutions has been detected in both cases: irradiation with light and sonication. Chae and colleagues demonstrated the presence of radicals in βC–halomethane solutions when these were irradiated with UV light. However, our experiments with DPPH clearly reveal the presence of radicals when βC–chloroform solutions were sonicated. Surprisingly the avidity for these radicals is greater in the βC case than in the DPPH case.

Finally, we wish to point out that, while it is necessary to irradiate for several hours with a mercury lamp to complete the reaction of formation of βC hydrochloride, by sonication in the same conditions only a few minutes are necessary to complete this reaction. Similar results are been observed for sonication of βC in alcoholic media. Therefore, it is necessary to pay attention when an ultrasonic bath is used, because ultrasonic radiation can modify strongly the properties of the media [5].

We propose βC as a probe to study in non-aqueous media the acidity that these can develop by sonication. Further work is in progress on this subject.

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