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Photocyclization of 2,6-dichlorodiphenylamines in solution

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ABSTRACT

The reactions of diclofenac, meclofenamic acid and 2,6-dichlorodiphenylamine were studied by pulsed and steady-state photolysis. The primary photoprocess of diclofenac is ring closure, the quantum yield of cyclization in dichloromethane and aqueous solution is Φ_{cyc} = 0.03 and 0.2, respectively. The results of the two related dichlorodiphenylamines are similar in the respect that the products are the corresponding 1-chlorocarbazoles and Φ_{cyc} is small in organic solvents and largest in aqueous solution.

1. Introduction

Diclofenac (Chart 1) is one of the most commonly used non-steroidal and anti-inflammatory drugs. However, it has also potentially harmful photosensitizing properties. Some fundamental photochemical features of diclofenac in solution have been reported [1–4]. The photodegradation of diclofenac in aqueous solution has been studied by various groups [5–14]. This is important for a better understanding of the UV treatment of wastewater [10]. The photodegradation of pharmaceuticals in aquatic environment has been reviewed [12]. The potential phototoxicity of diclofenac was ascribed to a biologically active photoproduct that is able to generate radicals upon photolysis, rather than to the parent drug [3,4]. Mechanistic studies indicate that the photochemistry of diclofenac involves electrocyclization to a monohalogenated carbazole [2–4]. In fact, 1-chlorocarbazole and carbazole are the respective initial and secondary photoproducts of 2,6-dichlorodiphenylamine (Cl_2DPA), which can be considered as the photoactive chromophore of diclofenac [3]. The photocyclization of 2,6-dichloroDPAs has been proposed to proceed via the triplet state [3,4]. For meclofenamic acid (*N*-(2,6-dichloro-*m*-tolyl)anthranilic acid: HO_2CCl_2DPA) which is another closely related amine, two cyclization products have been found [15]. A simplified mechanism of photoinduced ring closure of dichloroDPAs is illustrated in Scheme 1. The photoreactivity of 1-chlorocarbazole could be relevant to the understanding of the photobiological properties of diclofenac [1–4]. The photoreduction of 1-chlorocarbazole should be enhanced in the presence of an alcohol. Recently, the ozonation of diclofenac has been studied [7,16,17].

The photochemistry of diclofenac in solution may be compared to that of other diphenylamines, not containing chloro substituents. Parent diphenylamine (DPA), triphenylamine and *N*-methyldiphenylamine (MeDPA) have all been intensively studied by photochemical techniques [18–26]. They undergo an electrocyclic ring closure, and one rather unique property of DPAs is a photocyclization route in 4a,4b-dihydrocarbazoles via a triplet state [18–20]. The products of MeDPA are *N*-methylcarbazole (Scheme 2) and *N*-methyltetrahydrocarbazole, of which the latter is not stable and formed in deoxygenated solutions only [20]. The photocyclization of DPA has also been studied using thermal lensing [23] and time-resolved photoacoustic calorimetry [25]. A modified triplet state mechanism operates for the photoionization of DPA, when the two-pulse method is applied [24]. The photoinduced ring closure of DPAs in solution has recently been revisited and their oxygen uptake studied [26].

Here, the photochemistry of diclofenac was studied in several organic solvents and in aqueous solution. The effects of solvents, oxygen and pH concerning the quantum yield Φ_{cyc} of ring closure were outlined. These effects were compared with those of Cl_2DPA and HO_2CCl_2DPA, which are closely related to diclofenac since they also contain the 2,6-chloro substituents, see Chart 1. In fact, the 2-chloro group is a decisive element in the photocyclization of diclofenac. In contrast, the 1-carboxy group is not decisive, but the photoprocesses of meclofenamic acid (HO_2CMe_2DPA) and 2-carboxydiphenylamine (HO_2CDPA) differs from those of parent DPA.

2. Experimental

Diclofenac, 2-(2,6-dichloroanilino)phenylacetic acid, was from Heumann PSC [16]. The other compounds (EGA, Sigma)

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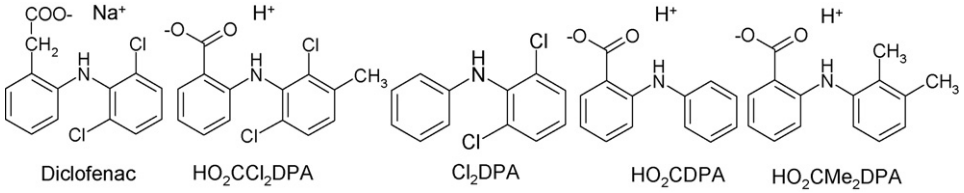
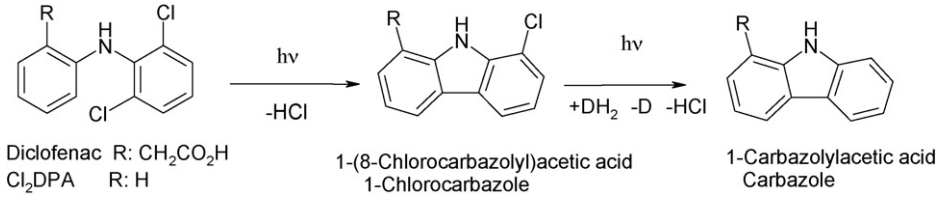
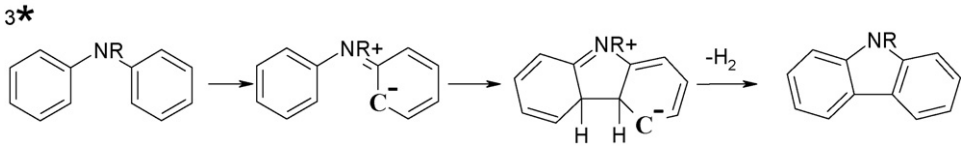


Chart 1.



Scheme 1.



Scheme 2.

were used as received after checking for impurities. Benzene, dichloromethane and acetonitrile (Merck) were Uvasol quality, water was from a millipore (milliQ) system. The absorption spectra were monitored on an UV/vis spectrophotometer (HP, 8453). The molar absorption coefficient of diclofenac in neutral water at 285 nm is $\varepsilon_{285} = 0.82 \times 10^4\,M^{-1}\,cm^{-1}$ [1], that of Cl_2DPA is $\varepsilon_{280} = 1.1 \times 10^4\,M^{-1}\,cm^{-1}$ [3]. In addition, HO_2CMe_2DPA and HO_2CDPA were briefly studied. Note that the solution of HO_2CCl_2DPA becomes opaque on addition of $HClO_4$ at pH 3. A spectrofluorimeter (Cary, eclipse) was employed to measure the fluorescence spectra. For photoconversion, a 1000-W high-pressure Hg–Xenon lamp and a monochromator were used for irradiation at 270–313 nm. Alternatively, a 200-W Hg lamp and suitable band-pass filter were used for irradiation at 313 nm. Irradiation at 254 nm (using a low-pressure Hg lamp) could be considered as an alternative. This is, however, limited by a too low conversion due to large absorption of the carbazole photoproduct at 254 nm, and was therefore not employed. For HPLC analyses a reverse phase ODS-3HD PerfectSilTarget 3 μm column (0.8 ml min^{-1}) with eluent gradient was used, the mobile phases were composed of 0.5% trifluoroacetic acid and either a 1:5 mixture of acetonitrile and water or neat acetonitrile. The dichloroDPAs and their main products have retention times of 17.6/16.7 19.0/17.2 and 18.7/19.1 min for diclofenac, Cl_2DPA and HO_2CCl_2DPA, respectively. The two product peaks for the latter [15] were not separated under our conditions. The quantum yield of cyclization was determined from plots of the absorption at appropriate wavelength or the HPLC signals vs dose using the aberchrome 540 actinometer for λ = 308/313 nm [27]. The experimental error of Φ_{cyc} is ±20%. The solutions were generally used without buffer and the initial pH was shifted by addition of protons ($HClO_4$) or hydroxyl ions; in a few cases buffers (<5 mM) were used. The oxygen concentration was measured by a Clark electrode (Hansatech). The relative yield of oxygen consumption was determined from the slope of $[O_2]$ vs irradiation time [28]. An excimer laser (Lambda Physik, EMG 201 MSC, pulse width of 20 ns and energy <100 mJ) was used for excitation at 308 nm. The absorption signals were measured with two digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling was used as in previous work [28]. The transient conductivity set-up was as used elsewhere [29]. All measurements refer to 24 °C.

3. Results

3.1. Photoconversion

The absorption spectrum of diclofenac in acetonitrile exhibits a maximum at λ_{DPA} = 282 nm, those of Cl_2DPA and HO_2CCl_2DPA have maxima at 280 and 320 nm, respectively. The absorbance of diclofenac at 282 nm decreases upon continuous irradiation at 313 nm or pulsed excitation at 308 nm, whereas those at maxima of the products, e.g. λ_C = 250 or 300 nm, increase markedly. Two or three isosbestic points (λ_i) result at low conversion, indicating a minor effect of secondary photolysis. The absorption spectra of diclofenac are similar in acetonitrile or methanol (Table 1). Generally, the spectral changes of each of the dichloroDPAs are comparable in methanol, water and their mixtures. Examples of these changes prior to and after UV photolysis are shown in Figs. 1–3 (insets) for diclofenac, HO_2CCl_2DPA and Cl_2DPA, respectively. The absorbances at λ_{DPA} decrease upon irradiation, whereas those at λ_C increase markedly. One major photoproduct of Cl_2DPA and diclofenac in polar solvents was detected by HPLC. The assignment to 1-chlorocarbazole and the corresponding derivative, respectively, is well established [1–4]. Likewise, the photoproducts of DPA or triphenylamine have the corresponding carbazole

Table 1
Spectral properties of dichloroDPAs[a].

	Diclofenac	Cl_2DPA	HO_2CCl_2DPA
λ_{DPA} (nm)	282	280[b]	340
λ_C (nm)	290, 340	290, 335[b]	305, 360
λ_i (nm)	268, 285, 305	266, 286, 300	320, 345
λ_f^{exc} (nm)	290, 338	290, 335	300, 365
λ_f^{em} (nm)	368	370	440

[a] In acetonitrile.
[b] Same values in methanol.

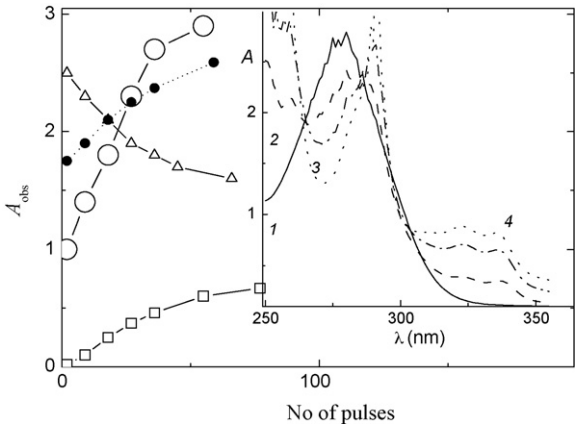


Fig. 1. Absorption at 255 nm (○) 280 nm (△), 295 nm (●) and 330 nm (□) of diclofenac in methanol–water (1:20) at pH 8 (open) and 3 (full) as a function of 308 nm excitation; inset: spectra at pH 8 and 0, 10, 50 and 150 pulses curves 1–4, respectively.

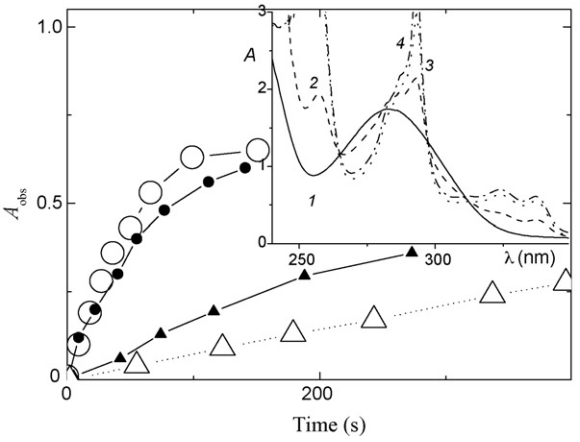


Fig. 2. Absorption at 330 nm of Cl_2DPA in benzene (△), acetonitrile (▲) and methanol–water (1:20) at pH 3 (●) and 12 (○) as a function of the time of irradiation at 313 nm; inset: spectra acetonitrile–water (1:1) at pH 7 and 0, 20, 50 and 200 s, curves 1–4, respectively.

structure [18–21]. The primary product from HO_2CCl_2DPA as corresponding carbazole is assumed by analogy.

The quantum yield Φ_d of substrate conversion was determined from plots of the spectral changes as a function of the irradiation time (Figs. 2, 3 and 5) or the number of 308 nm pulses (Figs. 1 and 4). Alternatively, the conversion into the major product from the HPLC chromatogram signals was used. The same photoconversion can be achieved by either continuous irradiation at 313 or 308 nm pulses. Thus, a low-intensity irradiation source is not a necessary precondition for cyclization. The Φ_{cyc} values were found to be equal to Φ_d for diclofenac in argon-saturated methanol–water (1:1). This demonstrates the minor role of side products. The photobehavior was found to be similar for Cl_2DPA and HO_2CCl_2DPA. The Φ_{cyc} values are compiled in Tables 2 and 3. Φ_{cyc} is not sensitive to oxygen, as the values are similar for the three dichloroDPAs in oxygen- and argon-saturated aqueous solution (see Fig. 2) or acetonitrile. Concerning the dependence of Φ_{cyc} on the nature of solvent a remarkably large effect was found in this work: Φ_{cyc} is relatively low in organic solvents and large in mixtures with water (Table 3). For diclofenac Φ_{cyc} depends somewhat on pH, which was varied from 3 to 12. This was also found for HO_2CCl_2DPA.

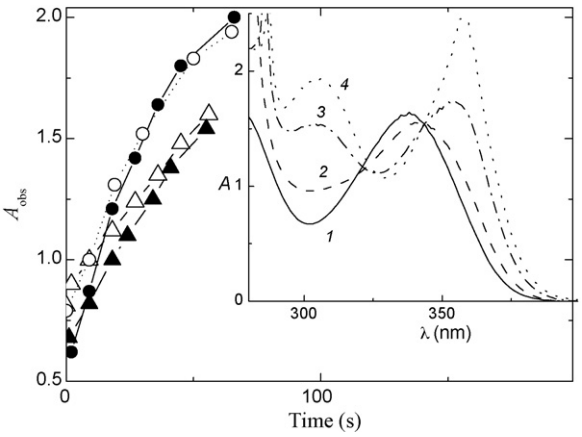


Fig. 3. Absorption at 300 (open) and 360 nm (full) of HO_2CCl_2DPA in acetonitrile (triangles) and methanol–water (1:1) at pH 7 (circles) as a function of the time of irradiation at 313 nm; inset: spectra at 0, 10, 30 and 90 s, curves 1–4, respectively.

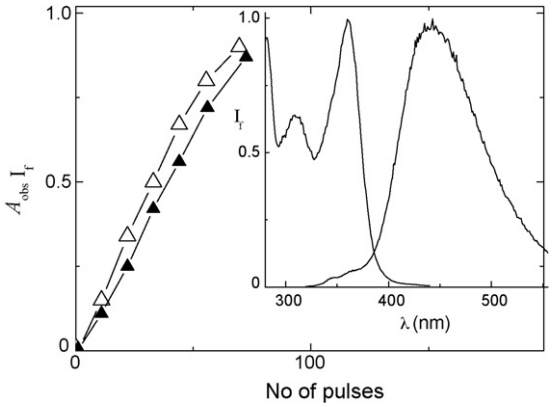


Fig. 4. Absorption at 295 nm (△) and fluorescence intensity at 440 nm (▲, λ_{ex} = 350 nm) of HO_2CCl_2DPA in methanol–water (1:5) as a function of the number of 308 nm pulses; inset: excitation and emission spectra after 200 pulses.

Table 2
Quantum yield Φ_{cyc} of cyclization of DPAs[a].

Compound	Oxygen	Air	Argon
Diclofenac	0.05	0.06	0.06
Cl_2DPA	0.06	0.06	0.06
HO_2CCl_2DPA	0.05	0.06	0.06
DPA[b]		0.22	
MeDPA[b]		0.45	0.28
Triphenylamine[b]		0.20	0.09

[a] In acetonitrile solution, λ_{irr} = 313 nm; no photoconversion (Φ_d < 0.01) for HO_2CDPA and HO_2CMe_2DPA.
[b] Taken from Ref. [26].

Table 3
Effects of solvent on the quantum yield Φ_{cyc} of cyclization of dichloroDPAs[a].

Solvent	Diclofenac	Cl_2DPA	HO_2CCl_2DPA
Benzene		0.02	
Dichloromethane	0.03	0.03[b]	0.03
Acetonitrile	0.06	0.06	0.05
MeCN–H_2O, 1:1	0.14	0.15	0.15
Methanol	0.05[b]	0.04	0.04
MeOH–H_2O, 1:1	0.16	0.16	0.14
Water, pH 3	0.18	0.25	0.20
Water, pH 8	0.18[b]		0.22
Water, pH 12	0.18	0.25	0.25

[a] In air-saturated solution, λ_{irr} = 313 nm; water: 5% methanol.
[b] Same values under argon.

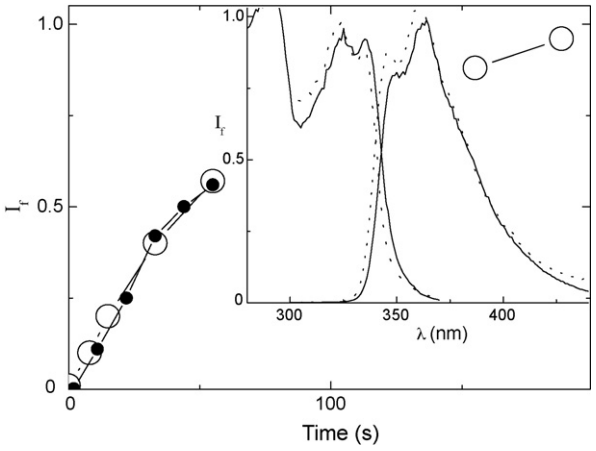


Fig. 5. Fluorescence intensity at 370 nm (λ_{ex} = 320 nm) of diclofenac (●) and Cl_2DPA (○) in methanol–water (1:5) as a function of the time of irradiation at 313 nm; inset: excitation and emission spectra of diclofenac (broken) and Cl_2DPA (full) after 100 s.

3.2. Excited singlet and triplet states

For the three dichloroDPAs almost no fluorescence was observed, the quantum yield is very small, $\Phi_f < 0.001$. This is in contrast to DPA or MeDPA, where $\Phi_f = 0.04$–0.05 [21]. The photoproducts of the three dichloroDPAs, however, show substantial fluorescence. The excitation maximum of the photoproducts of Cl_2DPA and diclofenac is at $\lambda_f^{exc} = 290$ nm, that of the emission is at $\lambda_f^{em} = 370$ nm, see Table 1. The fluorescence spectra of HO_2CCl_2DPA in methanol–water (1:4) at pH 6–8 are shown in Fig. 4, inset. The excitation spectra correspond to the absorption spectra and the excitation and emission spectra reflect a mirror relationship, especially those of the photoproducts of Cl_2DPA and diclofenac (Fig. 5, inset). The fluorescence spectroscopy of carbazole and N- and C-substituted carbazoles in homogeneous media has been reported [3]. For comparison, Φ_f of carbazole and *N*-methylcarbazole in nitrogen-saturated cyclohexane is 0.53 and 0.48, respectively [30]. The photoconversion can therefore also be determined by an increase of the fluorescence intensity signal. Examples of the intensity vs irradiation time are shown in Figs. 4 and 5. Note that the results from absorption and fluorescence coincide. Such a photoconversion with $\lambda_{irr} = 254$ nm has already been reported for diclofenac in aqueous acetonitrile [31]. Moreover, the intensity at 350 nm increases ca. 7 times upon addition of 2 mM α-cyclodextrin [13,14].

Excitation of DPA by 308 nm laser pulses produces the excited singlet and then the lowest triplet state, the latter has an absorption band around 500 nm. The *T*–*T* absorption maximum of DPA in methanol is at 530 nm, $\varepsilon_{530} = 1.5 \times 10^4\ M^{-1}\ cm^{-1}$ [21]. On the other hand, no triplet could be detected with diclofenac, Cl_2DPA and HO_2CCl_2DPA in acetonitrile. The absorption changes due to cyclization are faster than the pulse width of 20 ns, examples are shown in Fig. 6. The increase is observed in the 310–380 nm range for diclofenac and Cl_2DPA and ca. 15 nm red-shifted for HO_2CCl_2DPA. Moreover, no transient could be observed in other solvents, e.g. for Cl_2DPA in benzene or HO_2CCl_2DPA in water.

3.3. Transient conductivity

In aqueous solution at pH 5 and above diclofenac and HO_2CCl_2DPA are present as anions. A conductivity increase ($\Delta\kappa$: positive for increasing conductivity) was observed for both in argon-saturated aqueous solution at pH 6–8. Representative examples are shown in Fig. 7. The $\Delta\kappa$ signal increases within the width of the 308 nm laser pulse, decreases by 30–40% within 1 μs and then

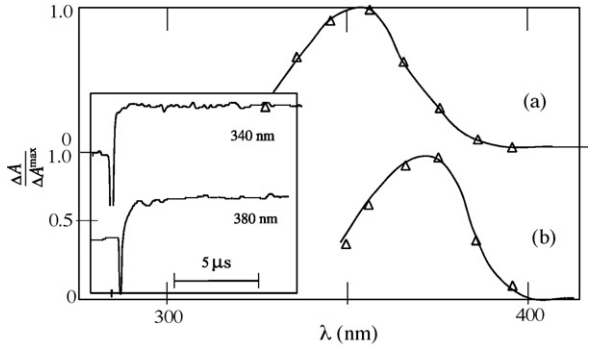


Fig. 6. Transient absorption spectra of (a) diclofenac and (b) HO_2CCl_2DPA in aqueous solution at pH 8 upon excitation with 308 nm pulses at 1 μs (△) after the 308 nm pulse; insets: kinetics at 340/380 nm.

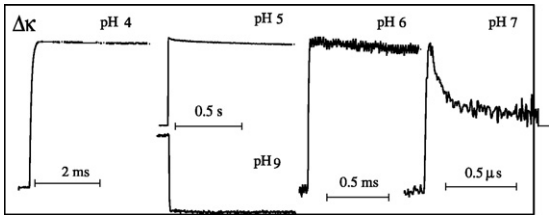


Fig. 7. Transient conductivity signals of diclofenac in aqueous (unbuffered) solution at pH 4–9 upon excitation with 308 nm pulses.

remains constant for at least one further second. The fast decay depends somewhat on the laser intensity. At pH 9–11 the conductivity signal decreases and remains negative in the ms–s range. The signal at 1 ms or even 1 s at pH 9–11 is ca. 0.6 of that at pH 6–8. This behavior is due to photoinduced proton and Cl^- formation. The equivalent conductivity of H^+ ($\Lambda = 350\ cm^2\ \Omega^{-1}\ mol^{-1}$) is ca. tenfold that of the Cl^- anion and the observed signal is therefore mainly that of the former species; diclofenac. When the OH^- concentration is increased up to pH 11 the permanent negative signal is due to proton consumption by neutralization. Note that for OH^- $\Lambda = 190\ cm^2\ \Omega^{-1}\ mol^{-1}$.

$$\text{diclofenac} + h\nu \rightarrow {}^{1*}\text{diclofenac} \rightarrow \text{1-chlorocarbazole-R} + H^+ + Cl^- \quad (1)$$

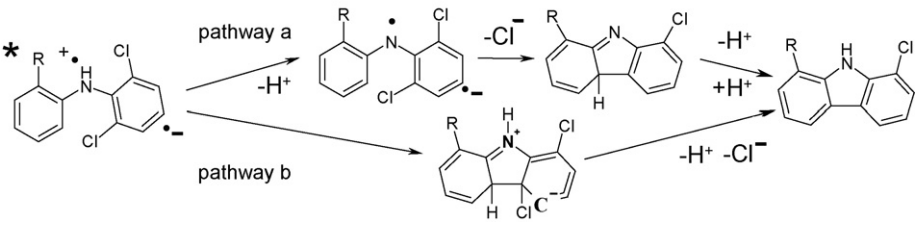
$$H^+ + OH^- \rightleftharpoons H_2O \quad (2)$$

H^+ and Cl^- are suggested to be formed from the dichloroDPAs within the laser pulse width and remain as conducting species unless the proton reacts with the hydroxide ion.

4. Discussion

4.1. Photochemistry of diclofenac

The phototoxicity of diclofenac should be ascribed to 1-chlorocarbazole, the biologically active photoproduct that is able to generate radicals upon photolysis [3,4]. The reactivity is determined by Φ_{cyc} which is in the range 0.03–0.2 (Table 2). $\Phi_{cyc} = 0.2$ with $\lambda_{irr} = 313$ nm for diclofenac in aqueous solution is in good agreement with the literature values, which are $\Phi_{cyc} = 0.22$, $\lambda_{irr} = 254$ nm at pH 7 in phosphate buffer [1]. $\Phi_{cyc} = 0.38$ for diclofenac at pH 6–7 and a slightly lower value for the protonated acid have also been reported, $pK_a = 4.2$ [10]. Previous studies demonstrate that the photochemistry of diclofenac involves cyclization to a monohalogenated carbazole [1–4]. In principle, cyclization could occur intramolecularly prior to or after photodechlorination. It could be assumed that the key species



Scheme 3.

associated with phototoxicity are the resulting aryl radicals. However, based on photophysical and photochemical studies on 1-chlorocarbazole, i.e. the model compound for secondary photochemistry, it has been proposed that the first photochemical reaction is a very rapid 6π-electrocyclization, and hence no radicals are formed at this stage [2–4].

A modified mechanism with charge separation is proposed in Scheme 3. The rate determining step is a fast hydrolytic dissociation or deprotonation. Cl^- elimination leads to a carbene. Subsequently, ring closure and a proton assisted aromatization can be considered. This is described by pathway (a). Alternatively, pathway (b) leads to a zwitterionic 4a-chloro-4b-hydrocarbazole derivative, its lifetime, however, must be shorter than 10 ns, since no transient could be detected. The carbazole is formed after release of Cl^- and H^+. The absence of any fluorescence for diclofenac [4] points to a much faster deactivation of the excited singlet state as first step in cyclization than for DPA or MeDPA, where $\Phi_f = 0.04$ [21]. No triplet could be detected for diclofenac in the solvents used. This is in contrast to DPA, where the triplet state has been characterized [21–26]. The results strikingly show that the cyclization is faster than a few ns (Fig. 5), in agreement with a singlet pathway. No photoinduced oxygen uptake was found for diclofenac in aqueous solution at pH 6–8 (not shown), in contrast to the cases of di- or triphenylamines [26]. This non-occurrence of oxygen uptake for diclofenac is also in agreement with a singlet pathway and supports a result from Moore et al. [1]. Interestingly, the oxidation of diclofenac with ozone yields quantitatively (95%) Cl^- [16], but the destruction efficiency of diclofenac is only 20% or less, as compared to 100% for olefins and ca. 50% for phenol [17].

A triplet pathway has been considered for diclofenac and the (vertical) triplet energies of the neutral diclofenac form and the deprotonated acid have been calculated to be 76 and 67 kcal mol^{-1}, respectively [11]. The much faster cyclization for diclofenac than in the DPA, MeDPA and triphenylamine cases is suggested to result from the heterolytic chloride release. The chloro and carboxy groups are not known to deactivate an excited molecule, without involving the triplet state. Also the solvent polarity should not markedly affect Φ_{isc} of carboxylic acids, which may reveal photoinduced decarboxylation [32,33], in contrast to diclofenac and HO_2CCl_2DPA.

4.2. Photochemistry of related dichlorodiphenylamines

Structurally, HO_2CCl_2DPA and Cl_2DPA are similar to diclofenac. Therefore, it would be expected that the photoreactions of the three dichloroDPAs are similar. They differ with regard to the alkyl group and by the fact that Cl_2DPA does not involve a charge in contrast to the two anilinophenylacetic acids. In fact, the Φ_{cyc} of diclofenac, HO_2CCl_2DPA and Cl_2DPA are similar (Table 3) and no triplet could be detected. Moreover, the absence of any fluorescence for dichloroDPAs points to a much faster cyclization than for parent DPA. The driving force for cyclization of excited HO_2CCl_2DPA and Cl_2DPA is suggested to be splitting of the C–Cl bond. Scheme 3 with charge separation would account for this mechanism of the two model compounds of diclofenac. The initial step is in agreement with the photoreduction of halogenated aniline, where an electron transfer and heterolytic release of the halogenide has been suggested [34]. One can expect that a photoinduced release of both Cl^- and H^+ from dichloroDPAs is favored in water and almost inhibited in solvents of low polarity. This is one reason for the dependence of Φ_{cyc} on the solvent polarity, which is similar for all three dichloroDPAs (Table 3). A comparison with the photolyzed 4-chlorophenol could be instructive since the elimination of HCl and a carbene intermediacy are also discussed [35].

4.3. Photoreactions of di- and triphenylamines

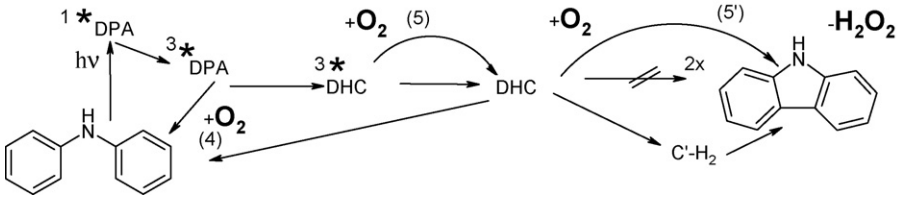
The observed triplet state of a diphenylamine converts into the triplet state of the corresponding 4a,4b-dihydrocarbazole (^{3*}DHC), when oxygen is excluded. ^{3*}DHC decays to the ground state which has a characteristic absorption maximum at 600 nm. Then DHC decays into the corresponding carbazole and tetrahydrocarbazole or a modified dihydrocarbazole (C′-H_2) [18–23]. Oxygen interferes threefold, it quenches ^{3*}DPA, ^{3*}DHC and DHC, steps (4), (5) and (5′). The lifetime of DPC in air- and argon-saturated solution is typically in the 0.1 and 1–30 ms range, respectively [26].

$$DPA(h\nu) \rightarrow {}^{1*}DPA \rightarrow {}^{3*}DPA \rightarrow {}^{3*}DHC \rightarrow DHC \rightarrow C'\text{-}H_2 \rightarrow \text{carbazole} \quad (3)$$

$$^{3*}DPA + O_2 \rightarrow DPA + O_2 \quad (4)$$

$$^{3*}DHC/DHC + O_2 \rightarrow \text{carbazole} + H_2O_2 \quad (5/5')$$

The rate constant for quenching the triplet of MeDPA in methylcyclohexane by oxygen is $k_{ox} = 3 \times 10^{10}$ M^{-1} s^{-1} [36]. The reactivity is lower for DPA in acetonitrile–water (1:1), $k_{ox} = 4 \times 10^9$ M^{-1} s^{-1} [26]. The photocyclization of DPA occurs via the triplet states ^{3*}DPA and ^{3*}DHC into DHC which is labile and reacts into carbazole and tetrahydrocarbazole. For DPA the mechanism is illustrated in Scheme 4.



Scheme 4.

The reaction patterns and kinetics of the photoconversion to carbazole have been discussed. The knowledge is much greater for MeDPA in non-polar media, where the quantum yield of intersystem crossing $\Phi_{isc} = 0.86$ and $\Phi_f = 0.04$ [21,22]. $\Phi_{cyc} = 0.4–0.7$ and 0.01–0.06 under air and in the absence of oxygen, respectively [19,22]; the calculated and observed quantum yields as a function of oxygen concentration are in good agreement. The maximum in a plot of Φ_{cyc} vs $[O_2]$ in the MeDPA/methylcyclohexane case is reached, when quenching of the ^{3*}DPA state and the 4a,4b-dihydrocarbazole are comparable, whereas at higher $[O_2]$ the latter process causes a decrease [36]. For DPA $\Phi_{isc} = 0.07$ and $\Phi_{cyc} = 0.05–0.1$ (under air) are lower in non-polar solvents, the oxygen effect on Φ_{cyc} is reversed, as $\Phi_{cyc} = 0.1$ in the absence of oxygen [18]. In polar solvents the difference due to *N*-substitution is smaller, based on $\Phi_{cyc} = 0.4–0.6$ in the absence of oxygen and $\Phi_{isc} = 0.86$ for DPA in methanol [21]. Thus, a dependence of Φ_{cyc} (in the presence of oxygen) and of Φ_{isc} on the solvent polarity is not obvious. For DPA the process is monophotonic even when a higher intensity is used, but a modified triplet state mechanism operates for the photoionization, when the two-pulse method is applied [26]. On the other hand, HO_2CDPA and HO_2CMe_2DPA, i.e. two carboxyDPAs not substituted by chloride groups, are not able to undergo photocyclization (see above). Apparently, the presence of a carboxy group in HO_2CDPA prevents photocyclization. It is worth mentioning that certain substituents at DPA hinder photocyclization [37]. The photodecarboxylative benzylation of phthalimide triplets with phenyl acetates has recently been studied [33]. Direct excitation of an aromatic carboxylate, e.g. phenylacetic acid, produces the excited singlet and then the lowest triplet state, which reacts via electron transfer. This seems to play no role for the two carboxyDPAs.

5. Conclusion

The photocyclization of diclofenac is sensitive to the polarity of the solvent. The quantum yields in acetonitrile and aqueous solution are $\Phi_{cyc} = 0.06$ and 0.2, respectively, and are only slightly lower than those of 2,6-dichlorodiphenylamine and meclofenamic acid.

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