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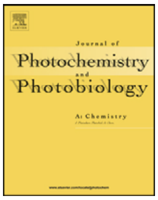

Photocleavage of dimers of coumarin and 6-alkylcoumarins

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ABSTRACT

The cleavage of four coumarin dimers, the *syn*-head-to-tail (ht) dimer of parent coumarin (*syn*-ht-CC**1**), the *anti*- and *syn*-hh dimers of 6-methylcoumarin (*anti*-hh-CC**2** and *syn*-hh-CC**2**, respectively) and the *anti*-hh dimer of 6-dodecylcoumarin (*anti*-hh-CC**3**), was studied by UV–vis and IR spectroscopy and HPLC upon direct 254 nm irradiation as well as sensitized excitation. The quantum yield of dimer splitting is $\Phi_{sp} = 0.1–0.3$ in various solvents and the effects of structure and solvent polarity are small. In certain solvents some of the dimers produced CO_2 along with the monomers in the splitting reaction. Electron transfer from dimers to the triplet state of sensitizers, such as benzophenone or 9,10-anthraquinone, was observed in acetonitrile.

1. Introduction

The photodimerization properties of parent coumarin (C**1**) in solution as well as in solid systems have been intensively investigated [1–9]. Four photodimers (CC), *syn*-head-to-head (*syn*-hh), *anti*-hh, *syn*-head-to-tail (ht) and *anti*-ht, were identified for C**1** and a series of 6-alkyl coumarins, e.g. 6-methylcoumarin (C**2**) and 6-dodecylcoumarin (C**3**) [10], see Scheme 1. Essentially *syn*-hh and *anti*-hh dimers and virtually no *anti*-ht dimers are formed upon direct excitation of C**1** in solution. The *anti*-hh dimers of C**1** and C**2** were found after benzophenone sensitization in both polar and non-polar solvents and *anti*-hh dimers are favoured in solvents of low polarity, but *syn* dimer formation is enhanced in polar solvents and micellar solutions of cationic cetyltrimethylammonium bromide and anionic sodium dodecyl sulfate [10].

The photophysical properties of coumarins are in favour of an overall triplet mechanism rather than of separate singlet and triplet pathways for the non-sensitized and sensitized photodimerizations of coumarins, respectively [11–16]. Fluorescence and phosphorescence of C**1** were detected at −196 °C, but virtually no emission appears in fluid solution, the quantum yield of fluorescence is $\Phi_f < 10^{-3}$ [13]. The triplet state is observable at room temperature [14–16], the T–T absorption spectra of C**1**, C**2** or C**3** have maxima at 410–430 nm and the influence of substitution on the quantum yield of intersystem crossing Φ_{isc} in a given solvent is small at room temperature. $\Phi_{isc} = 0.054$ for C**1** in water [15], smaller for C**1** and C**2** in most other solvents and largest in 2,2,2-trifluoroethanol (TFE) [13]. The dimerization quantum yield (Φ_{dim}) upon irradiation at 300–350 nm is very low in most cases, e.g. for C**1** (0.3 M) in dichloromethane and acetonitrile (for *syn*- and *anti*-hh) $\Phi_{dim} = 1 \times 10^{-3}$ and 9×10^{-4}, respectively [5,8]. On the other hand, Φ_{dim} is large, up to 0.8, for the BF_3/OEt_2 catalyzed reaction [9]. Recently, several points in the mechanism of photodimerization were addressed, e.g. the roles of the sensitizer, solvent and molecular structure, and reasons for the differing triplet reactivities were discussed [12]. The dimers are photocleaved into monomers upon irradiation at 200–300 nm (Scheme 1). The dimer splitting of coumarins is efficient [12,17–20] and for dimers of C**1**, which were prepared by benzophenone-sensitized irradiation in 2-propanol, a quantum yield of $\Phi_{sp} = 0.2$ has been reported upon irradiation at 266 nm [17].

Photoswitched storage and release of guest molecules in the pore void of coumarin-modified MCM-41 nanoparticles has been reported [21]. Reversible photocleavage and crosslinking was achieved when 4-methylcoumarin was functionalized in polyester [22]. With respect to the wavelength dependence of photodimerization versus photocleavage, the features of coumarins appear to be analogous to the thymine and other pyrimidine moieties. The photosensitized splitting of thymine dimers has been achieved by using a variety of sensitizers, mostly electron acceptors, such as

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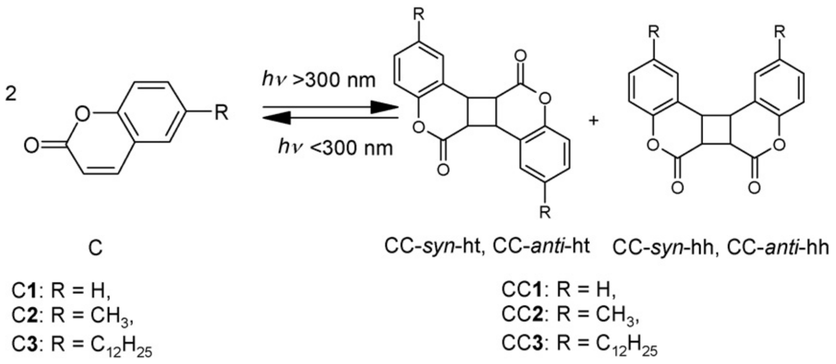


Scheme 1.

quinones or flavins [23–30]. Photoinduced DNA repair and splitting of pyrimidine model dimers can also be initiated by electron transfer [23]. The photoinduced electron transfer of monomers has been reviewed [31]. For cyanine dyes it has been shown that the triplet state of both, monomer and dimer, can be quenched by electron donors and acceptors [32].

Here, we aim at a deeper insight with regard to the photochemical dimer splitting of parent C**1** and alkylcoumarins. For these purposes, *syn*-ht-CC**1**, *anti*-hh-CC**2**, *syn*-hh-CC**2** and *anti*-hh-CC**3** dimers were studied by both UV and IR spectroscopy in the absence and presence of appropriate sensitizers using illumination at 248/254 and 308 nm, respectively. As sensitizers benzophenone, 4-carboxybenzophenone, duroquinone (Me_4BQ), chloranil (Cl_4BQ) and 9,10-anthraquinone (AQ) were used.

2. Experimental details

The coumarins were from previous work [12] and the sensitizers as commercially available. The solvents (Merck) were checked for impurities. For irradiation at 254 and 280/366 nm a Hg lamp and a 1000 W Hg–Xe lamp with a monochromator was used, respectively. The UV–vis spectra were recorded on a diode array (HP 8453). They are presented for 0.5 mm pathlength, otherwise performed in 1 cm cells. The quantum yield Φ_{sp} was measured using the absorption at the maximum versus irradiation time. As reference uridine in water was used, $\Phi_{\mathrm{d}} = 0.002$ [33]. For HPLC analyses a 125 × 4.6 mm Inertsil ODS-3 5 μm column was used with MeOH–water 1:2 or 2:1 as eluents. Redimerization can be excluded since the monomer concentrations derived from dimer splitting are as low as 0.2 mM. Photoproduct analyses after 366 nm irradiation of AQ or Cl_4BQ, in acetonitrile–water (1:1) in the presence of *syn*-ht-CC**1** in using HPLC were performed, but not further carried out since they revealed several peaks related to quinone photochemistry and overlapping with the coumarin monomer and dimer signals. The molar absorption coefficient of monomeric C**1** in acetonitrile at 310 nm is $\varepsilon_{310} = 5.2 \times 10^3\ \mathrm{M^{-1}\,cm^{-1}}$ [20]. The value of C**2** in several solvents at the maximum is typically $\varepsilon_{275} = (0.8\text{–}1.2) \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$ and for the dimers *anti*-hh-CC**2** and *syn*-hh-CC**2** in chloroform $\varepsilon_{280} = 3.1 \times 10^3$ and $\varepsilon_{280} = 2.5 \times 10^3\ \mathrm{M^{-1}\,cm^{-1}}$, respectively [10]. The IR spectra were recorded on a FTIR spectrometer (Bruker IFS66); the concentrations were adjusted to $A_{\mathrm{exc}} = 0.1\text{–}2$ in 0.05 cm CaF_2 cells. The molar absorption coefficient of *anti*-hh-CC**2** in methylcyclohexane (MCH) was estimated as $\varepsilon_{1722} = 5 \times 10^3\ \mathrm{M^{-1}\,cm^{-1}}$. For photolysis with UV–vis detection two excimer lasers ($\lambda_{\mathrm{exc}} = 248$ and 308 nm, rise time 10–20 ns), two transient digitizers (Tektronix 7912AD and 390AD) and an Archimedes 440 computer for data handling were used as in previous work [11]. The measurements refer to 25 °C.

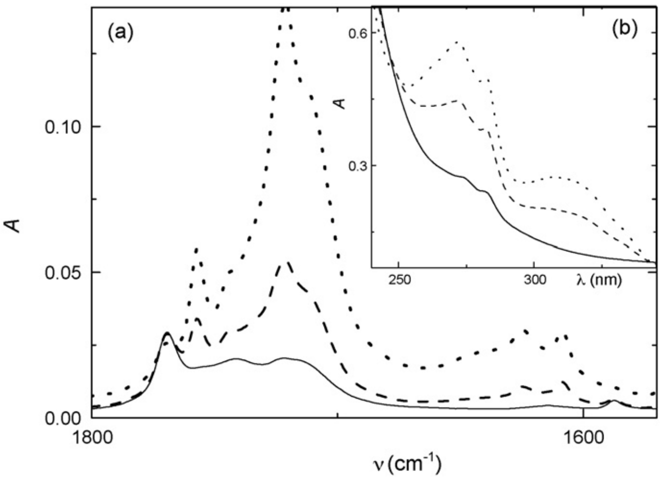


Fig. 1. (a) IR and (b) corresponding UV spectra of *syn*-ht-CC**1** in air-saturated MCH prior to (full) and after 2 (dashed) and 10 min (dotted) irradiation at 254 nm.

3. Results and discussion

3.1. Direct photocleavage of dimers

The absorption spectrum of *syn*-ht-CC**1** in MCH (Fig. 1b), carbon tetrachloride or more polar solvents has a maximum at 275 nm and no band above 300 nm. Continuous UV irradiation results in an absorption increase at 250–350 nm and an isosbestic point at 248 nm. The spectral changes with stronger absorbance at a major maximum around 275 nm and minor maximum at 312 nm are due to monomer formation. Corresponding spectra were obtained in solvents of low and large polarity for the other coumarin dimers, the changes are shown for *anti*-hh-CC**2** in acetonitrile and *anti*-hh-CC**3** in MCH, Figs. 2b and 3b, respectively.

The IR spectra of monomeric C**1** and dimeric *syn*-ht-CC**1** in MCH exhibit major peaks at $\tilde{\nu}_m = 1730\ \mathrm{cm^{-1}}$ and $\tilde{\nu}_d = 1757\ \mathrm{cm^{-1}}$, respectively (Fig. 1a). *Anti*-hh-C**2** in air-saturated MCH shows a major dimer peak at $1780\ \mathrm{cm^{-1}}$, an isosbestic point at $1769\ \mathrm{cm^{-1}}$ and the monomer band centered at $\tilde{\nu}_m = 1722\ \mathrm{cm^{-1}}$ (not shown). Additional monomer peaks appear at 1575, 1497, 1170, 1125 and $1044\ \mathrm{cm^{-1}}$. The main absorption peak of *anti*-hh-CC**2** in carbon tetrachloride is similar and shifted to $\tilde{\nu}_d = 1768\ \mathrm{cm^{-1}}$ in more polar solvents, acetonitrile (Fig. 2a). For *anti*-hh-CC**3** in MCH the peak at $\tilde{\nu}_d = 1779\ \mathrm{cm^{-1}}$ converts to the monomer peak with $\tilde{\nu}_m = 1722\ \mathrm{cm^{-1}}$ (Fig. 3a). Corresponding spectra were obtained for other cases (Table 1). The peak to peak ratio $2 \times \varepsilon_{\mathrm{m}}/\varepsilon_{\mathrm{d}}$ of monomers at $\tilde{\nu}_m$ (after complete cleavage) to dimers at $\tilde{\nu}_d$ of 0.4–0.9 was obtained. The photoproduct of *anti*-hh-CC**2** in carbon tetrachloride and dichloromethane, however, is not fully in line with the

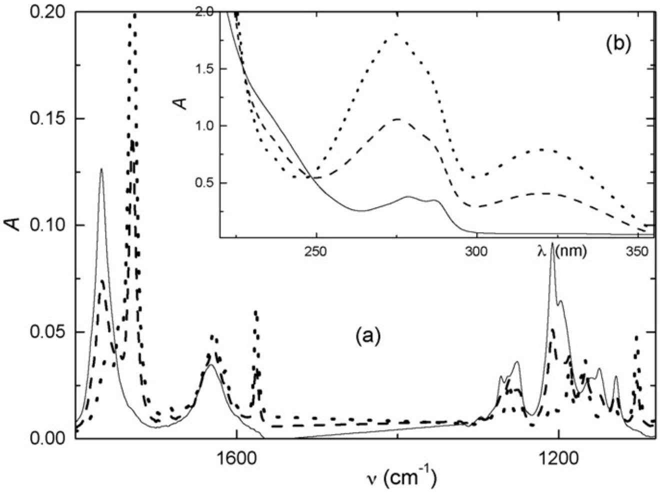


Fig. 2. (a) IR and (b) UV spectra of *anti*-hh-CC**2** in air-saturated acetonitrile prior to (full) and after 2 (dashed) and 10 min (dotted) irradiation at 254 nm.

monomers in other solvents, indicating a side reaction with the solvent.

3.2. Quantum yield

Examples of the photoconversion as a function of irradiation time are shown in Fig. 4 using λ_{irr} = 254 nm. The quantum yield is Φ_{sp} = 0.15–0.28 (Table 1). A value of Φ_{sp} = 0.21 in acetonitrile has been reported upon irradiation at 266 nm of a coumarin dimer mixture [20]. The initial absorption at 270 nm is much weaker than that of the two monomers, as expressed by the ratio ε_d(UV)/2 × ε_m(UV) = 0.2–0.3. The identity of the coumarin dimers has been documented previously [10]. The postulated excited state as intermediate in direct excitation is a non-fluorescent singlet state since an observation of the triplet state in the ns–μs range failed. Note that the triplet state of monomers has been detected [11,12,14]. Fast dimer splitting bypassing the lowest triplet state is supported by the observation that the change in absorbance at 280–320 nm, measured by laser flash photolysis upon direct excitation at 248 nm, is completed within the pulse width of 10 ns (not shown). The splitting probably takes place in picoseconds, i.e. instantaneously and without detectable intermediate. The mechanism of direct cleavage of the dimer could occur via a biradical (Scheme 1) or, less likely, via radical ions.

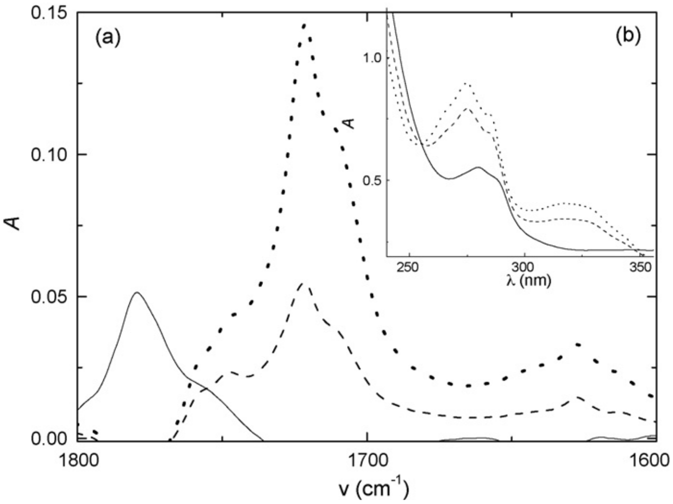


Fig. 3. (a) IR and (b) UV spectra of *anti*-hh-**3** in air-saturated MCH prior to (full) and after 2 (dashed) and 10 min (dotted) irradiation at 254 nm.

Table 1
Monomer and dimer IR maxima of **1**–**3** and qantum yield of splitting[a].

Dimer	Solvent	Φ_{sp}	$\tilde{\nu}_d$ (cm^{-1})	$\tilde{\nu}_m$ (cm^{-1})
syn-ht-CC**1**	MCH		1768	1722
	CCl$_4$[b]	0.15	1757	1730
	Dichloromethane		1757	1732
	Acetonitrile		1760	1735
anti-hh-CC**2**	Cyclohexane	0.28	1780[c]	1722[c]
	CCl$_4$		1778	1746
	Chloroform	0.2	1766	1726
	Dichloromethane	0.2	1766	1726
	Acetonitrile	0.2	1768	1730
anti-hh-CC**3**	MCH		1779	1722
	CCl$_4$	0.18	1776	1741
	Dichloromethane		1766	1727

[a] In air-saturated solution, λ_{irr} = 254 nm.
[b] Using λ_{irr} = 290 nm.
[c] Using MCH.

3.3. Side reaction

Irradiation at 254 nm generally gives rise to a decrease in dimer absorption and formation of new peaks of the monomers (and/or other minor photoproducs). For dimeric *anti*-ht-CC**1** or *anti*-hh-CC**2** in MCH or CCl$_4$ (and to a smaller extent for *anti*-ht-CC**1** in acetonitrile) also a photoinduced peak at 2340 cm^{-1} appears. It is formed in proportion to irradiation time in a similar manner to the monomer peaks and is assigned to CO$_2$ formation. The estimated yield is smaller than 15%, taking an absorption coefficient of $\varepsilon_{2240} = 1.5 \times 10^4$ M^{-1} cm^{-1} for CO$_2$ with respect to $\varepsilon_{1722} = 5 \times 10^3$ M^{-1} cm^{-1} for C**1**. For *anti*-ht-CC**1** in acetonitrile under otherwise the same conditions the CO$_2$ peak is 20 times smaller than in MCH. The photodecarboxylation of coumarin dimers concomitant to photocleavage is new and without precedence in the literature. Speculative reactions of hh and ht dimers leading to CO$_2$ are proposed in Scheme 2, but these need further investigations for verification. It should be mentioned that a new type of photodimerization reaction with release of CO$_2$ has been reported for certain coumarin derivatives, which, however, are carboxy-substituted [34], in contrast to parent C**1** or C**2**, where CO$_2$ is only part of the skeleton. This cannot support photodecarboxylation of coumarin dimers as a general phenomenon.

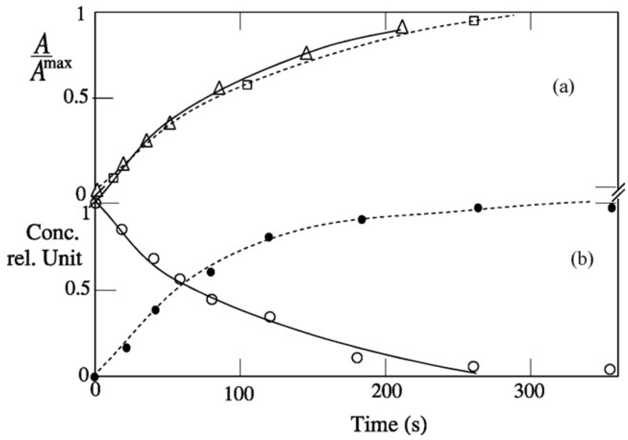
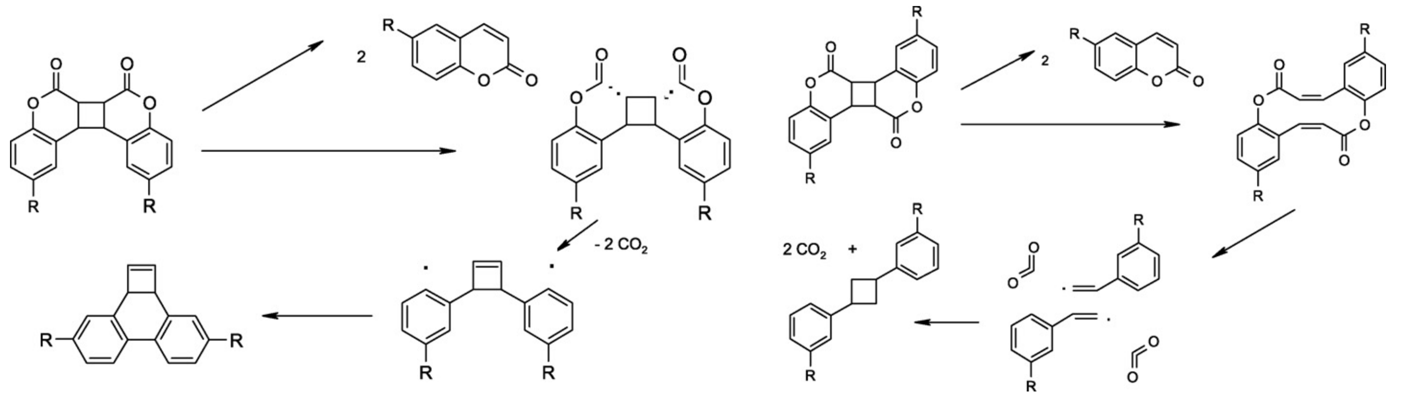


Fig. 4. Plots of (a) absorption at 320 nm versus time of irradiation at 254 nm for splitting of *syn*-ht-CC**1** and (b) monomer (full) and dimer (open) concentrations using HPLC analyses in argon-saturated cyclohexane (circles), carbon tetrachloride (triangles) and acetonitrile (squares), pathlength 1 cm.



Scheme 2.

3.4. Photoreactions of coumarin monomers

The photodimerization properties of C**1** and 6-alkylcoumarins were recently discussed [11]. Variation of the concentration changes the triplet lifetime (τ_T) and reveals a quenching reaction of the triplet state of the monomer (^{3*}C) by the ground state (1) in competition to intrinsic decay. The postulated complex $^{3*}C\cdots C$ which is not observable under our conditions is the precursor of dimers and α is a fraction between 0 and 1.

$$^{3*}C + C \rightarrow {}^{3*}C\cdots C \rightarrow \alpha CC + (1-\alpha)2\times C \text{ or other products} \tag{1}$$

The low quantum yield of dimerization of C**1** or C**2** is partly due to the small Φ_{isc} value [5,8,11]. Φ_{isc} = 0.03–0.06 in dichloromethane, smaller in benzene, acetonitrile or methanol and larger in TFE and water [11]. For reaction (1) to initiate non-sensitized dimerization, a concentration of 1 mM is necessary for 50% triplet quenching in dichloromethane or acetonitrile, but in water 0.03 mM coumarin is sufficient to populate the ^{3*}C state and to successfully compete with triplet decay without quenching. Changes in the product pattern could be due to larger preorientation of complex-hh versus complex-ht in competition to intrinsic decay. We propose three products pathways, taking that for *anti*-ht as absent. In these three cases, the final dimer formation competes with non-reactive decay into two coumarin molecules (Scheme 1). Calculations support the triplet route into the *anti*-hh dimer [35].

3.5. Oxidative photosensitized dimer cleavage

On addition of *anti*-hh-CC**2** the triplet lifetime τ_T of benzophenone in acetonitrile at the maximum λ_{TT} = 520 nm becomes shorter, the T–T absorption spectrum is not markedly changed, but no acceptor triplet was found (Fig. 5a). The rate constant for triplet quenching, obtained from the slope of the linear dependence of $1/\tau_T$ versus the *anti*-hh-CC**2** concentration, is $k_q = 0.8\times10^9\ M^{-1}\ s^{-1}$. In the presence of water at pH 12 the triplet lifetime is also shorter, however, the radical anion of the sensitizer ($S^{\bullet-}$) with a major band at 320 nm and a weaker band at 600 nm was detected as long-lived species (triangles in Fig. 5b). The results for 4-carboxybenzophenone are $k_q = 1.1\times10^9\ M^{-1}\ s^{-1}$ in acetonitrile–water (1:1) and the spectra in alkaline solution are similar (Fig. 5c). The photosensitized cleavage of coumarin dimers could occur via energy transfer from ^{3*}S (3). With benzophenone and 4-carboxybenzophenone, however, this can be excluded. Instead, electron transfer (4) takes place, i.e. formation of $S^{\bullet-}$ and the cationic dimer radical, $CC^{\bullet+}$. The likely possibility is instantaneous cleavage of the dimeric radical cation (5) and back electron transfer via (6) see Scheme 3.

$$S + h\nu \rightarrow {}^{1*}S \rightarrow {}^{3*}S \tag{2}$$

$$^{3*}S + CC \rightarrow {}^{3*}S\cdots CC \rightarrow S + CC \text{ or } 2C \tag{3}$$

$$^{3*}S + CC \rightarrow S^{\bullet-} + CC^{\bullet+} \tag{4}$$

$$CC^{\bullet+} \rightarrow C + C^{\bullet+} \tag{5}$$

$$S^{\bullet-} + C^{\bullet+} \rightarrow S + C \tag{6}$$

When benzophenone in dry acetonitrile was applied (Fig. 5a), $S^{\bullet-}$ could not be detected probably due to too fast electron back transfer in the solvent cage. This is in contrast to the alkaline medium (Fig. 5b). An example of inefficient quenching is naphthalene, where the triplet is kinetically observed, but no quenching reactivity by *anti*-hh-CC**2** was found (not shown).

Quinones are also appropriate electron acceptors. The T–T absorption spectrum of AQ has λ_{TT} = 360 nm and the triplet lifetime in acetonitrile is ca. 10 μs. In the presence of *anti*-hh-CC**2** τ_T becomes shorter (Fig. 6a) and the rate constant is $k_q = 3\times10^9\ M^{-1}\ s^{-1}$. With AQ in acetonitrile–water (1:1) a transient with maximum at 500 nm was formed (Fig. 6b) which is assigned to the radical anion ($AQ^{\bullet-}$) [36]. The lack of $AQ^{\bullet-}$ formation in dry acetonitrile (Fig. 6a) is suggested to be due to electron back trans-

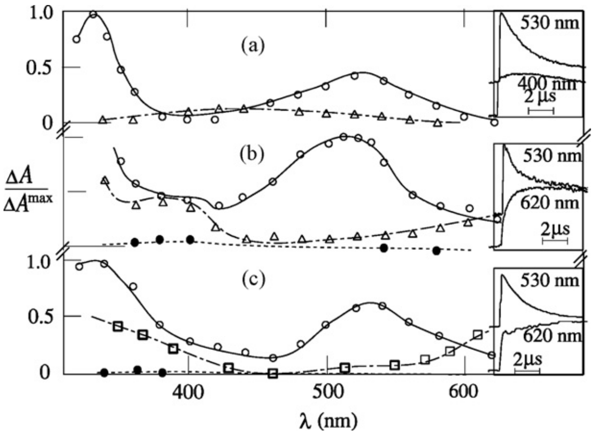
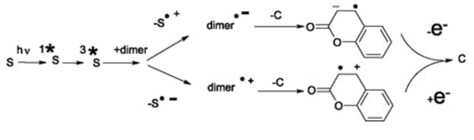


Fig. 5. Transient absorption spectra (under argon) in the presence of *anti*-hh-CC**2** (0.3 mM) of benzophenone (a) in acetonitrile and (b) in acetonitrile–water (1:1) at pH 12 (b) and (c) of 4-carboxybenzophenone in aqueous solution at pH 12 at 20 ns (○), 1 μs (△) and 10 μs (□) after the 308 nm pulse; insets: kinetics as indicated.



Scheme 3.

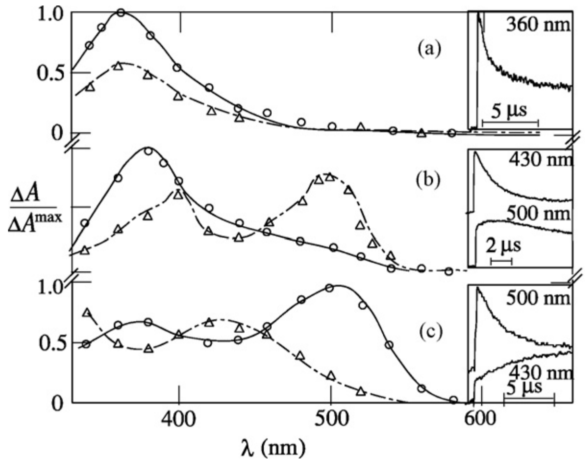


Fig. 6. Transient absorption spectra (under argon) of AQ in (a) acetonitrile and (b) acetonitrile–water (1:1) and (c) of Cl_4BQ in acetonitrile–water (1:1) in the presence *anti*-hh-CC**2** (mM) at 20 ns (○) and 1 μs (△) after the 308 nm pulse; insets: kinetics as indicated.

fer in the solvent cage, as for benzophenone. The rate constant for quenching of triplet Me_4BQ by *anti*-hh-CC**2** dimers is lower, $k_q = 1 \times 10^9\ M^{-1}\ s^{-1}$. For Cl_4BQ as sensitizer, the triplet quenching at $\lambda_{TT} = 520$ nm occurs with $k_q = 1.5 \times 10^9\ M^{-1}\ s^{-1}$. Formation of $Cl_4BQ^{\bullet-}$ with maxima at 330 and 420 nm (Fig. 5c) via reaction (4) indicates cationic dimer cleavage. To summarize, we observed formation of the radial anions of appropriate sensitizers but failed to detect the corresponding radical cation of the dimers. Their yield is expected to be the same as that of the cationic counterpart, but their molar absorption coefficients are lower than our detection limit. We also failed to detect a reductive dimer cleavage. For this purpose we employed a ruthenium complex, $Ru(bpy)_3{}^{2+}$ as photosensitizer, where quenching was found to occur with $k_q = 1 \times 10^9\ M^{-1}\ s^{-1}$.

3.6. *Comparison with pyrimidine dimers*

The sensitized photocleavage of thymine and other pyrimidine dimers is known to proceed via electron transfer from excited electron donors or acceptors [23–30]. The cleavage of the dimeric radical cation splits instantaneously. As electron acceptors AQ derivatives [23,24] and flavin derivatives [29] were applied in the oxidative photosensitized dimer cleavage. The cationic pyrimidine dimer radical is instantaneously cleaved and the monomeric radical cation reacts with $S^{\bullet-}$ via back electron transfer, Scheme 3. The reductive cleavage was also reported. As electron donors in the reductive photosensitized dimer cleavage indol derivatives [26], *N*,*N*-dimethylaniline [28] or *N*,*N*,*N*,*N*-tetramethylbenzidine [29] were applied. The anionic dimer radical is instantaneously cleaved into the monomeric radical anion which reacts via back electron transfer, analogously to Scheme 3.

4. Conclusions

The photochemical cleavage mechanism of coumarin dimers was studied. The direct cleavage of the dimers is characterized by a relatively high quantum yield $\Phi_{sp} = 0.2$ and a fast reaction upon direct irradiation at 248 and 254 nm. The photocleavage is suggested to occur via a non-fluorescent short-lived singlet state. The oxidative cleavage, due to electron transfer from the dimer to the triplet state of an acceptor, was achieved with ketones, such as benzophenone or quinones, e.g. chloranil or 9,10-anthraquinone. CO_2 formation upon direct irradiation was observed along with the expected monomers for *anti*-ht-CC**1** or *anti*-hh-CC**2** in MCH or CCl_4 and for *anti*-ht-CC**1** in acetonitrile.

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