

PHOTOREACTIONS OF DERIVATIVES OF 2-PHENYLINDAN-1,3-DIONE IN POLAR AND NON-POLAR SOLVENTS

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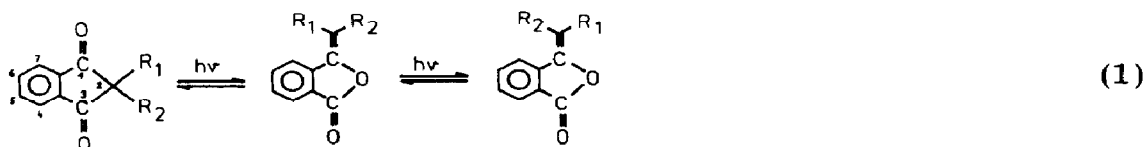
Summary

Two primary photoreactions were observed for derivatives of 2-phenylindan-1,3-dione in various solvents: (1) cleavage of the hydrogen atom in the α position to both keto groups resulting in the formation of 2-arylundan-1,3-dion-2-yl radicals; (2) photoisomerization to benzylidenephthalides as a result of bond rupture via a Norrish type I mechanism. Both processes are possible with different quantum yields from the diketo form (in apolar solvents), from the enol form (in alcohols) and from the enolate form (in alkaline water).

1. Introduction

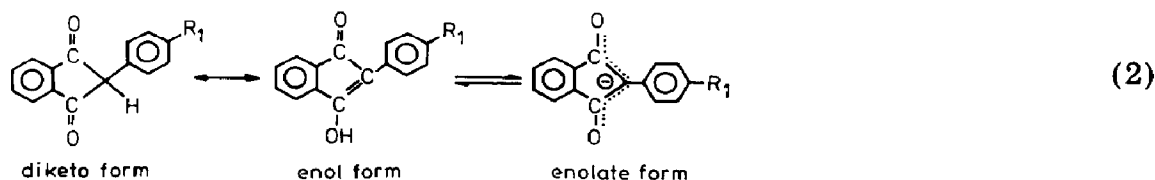
The derivatives of 2-arylundan-1,3-dione are of particular technological interest as inhibitors of autoxidation processes in the liquid phase, as stabilizing agents for polymers and as regulators in polymerization reactions [1]; these effects require the participation of free radicals. Many of these derivatives are, moreover, physiologically active; they influence the central nervous system or show an anticoagulant action similar to that of coumarins [2]. Some of them are also used to modify amino acids and peptides [3].

The photoisomerization of substituted indandiones leads to γ -lactones which are derivatives of benzylidenephthalide [4 - 7]. Mixtures of isomers in photostationary equilibrium are obtained using various substituents R_1 and R_2 [4]:



In addition to this photoisomerization, a photoinduced dimerization has also been observed at position 2. One moiety of the dimer may additionally photoisomerize as described above [6, 8].

The UV absorption of 2-phenylindandione derivatives depends on the distribution of several tautomeric forms [9, 10]. These are the diketo form prevailing in apolar solvents (responsible for a $\pi\pi^*$ band at $\lambda \approx 220$ nm and a weak $n\pi^*$ band around 300 nm in cyclohexane) and the enol and enolate forms which produce additional absorption bands in the UV and visible range in polar media (alcohols, acetonitrile and alkaline water):



No systematic investigations concerning the photochemical properties of these tautomeric forms have been carried out to date. It was therefore of interest to study the transients and products of the photolysis of the individual forms under both flash and stationary conditions. In addition to the processes of photoisomerization and photodimerization already known, the possibility of the photoejection of solvated electrons e_{aq}^- in aqueous alkaline solution has also been considered [11, 12]. In order to obtain more information about the processes involved, the results are compared with semi-empirical quantum chemical calculations performed using the Pariser-Parr-Pople self-consistent field configuration interaction (PPP-SCF-CI) method.

2. Experimental details

Two types of equipment were used for the flash photolysis measurements.

(a) Equipment from Applied Photophysics (London) was used to provide flashes with a pulse length of 10 μ s at a power of 200 - 800 J. The analysing light was obtained from a tungsten-halogen lamp (100 W) or a high pressure xenon lamp (200 W). The data were processed using a multi-channel analyser (KFK Budapest) connected to a printer and a plotter.

(b) Equipment from Northern Precision was modified to provide flashes with a pulse length of 7 μ s at a power of 20 - 200 J. A photomultiplier (Hamamatsu R 955) or a photodiode (Siemens BPW 34) was used for detection. The transients were displayed on a storage oscilloscope (Tektronix 7623 A).

Stationary irradiation was carried out using either a 450 W high pressure xenon lamp in combination with a high intensity monochromator (Schoeffel Kratos) or a low pressure mercury lamp ($\lambda = 254$ nm; the 185 nm line was

eliminated using a 1 M aqueous methanol filter). The irradiation vessels are described elsewhere [13,14]. A thermoelectric measuring device (YSI-Kettering model 65A radiometer) in combination with chemical actinometry (potassium tris(oxalato)ferrate(III) [15] with quantum yield $Q(\text{Fe}^{2+}) = 1.25$ at 220 and 254 nm [15, 16], $Q(\text{Fe}^{2+}) = 1.24$ at 285 nm and $Q(\text{Fe}^{2+}) = 1.23$ at 330 and 340 nm [15]) was used to determine the light intensities at various wavelengths. The fluorescence spectra were measured using a modified Zeiss ZFM4C fluorometer and the absorption spectra were obtained using a Perkin-Elmer-Coleman 575 spectrophotometer.

The indandione derivatives 2-(4'-dimethylaminophenyl)-indan-1,3-dione (DAPI) and 2-(4'-methoxyphenyl)-indan-1,3-dione (MPI) were synthesized by condensing the phthalide with substituted benzaldehydes [17 - 19]. DAPI was purified by repeated recrystallization from benzene (melting point, 190 - 191 °C), and MPI was purified by recrystallization from ethanol (melting point, 151 - 152 °C). Both substances were shown to be homogeneous by thin layer chromatography tests. Other chemicals were reagent grade (E. Merck, Darmstadt), and the solvents for fluorescence measurements were fluorescence grade. Water was distilled four times. Unless stated otherwise, the solutions were purged with argon.

Chloroacetate was used as a scavenger for solvated electrons [20]. The scavenging reaction yields Cl^- which was determined spectrophotocchemically using Hg^{2+} and diphenylcarbazone [21].

The optimization and parametrization of the geometry for the PPP-SCF-CI calculations are described elsewhere [22].

3. Results

3.1. UV absorption spectra

The absorption spectra of solutions of DAPI and MPI in cyclohexane, ethanol and alkaline water are displayed in Figs. 1 and 2.

3.2. Flash photolysis experiments

The transient absorption spectra obtained on flashing solutions of DAPI in cyclohexane, ethanol and alkaline water are shown in Fig. 3 and Table 1.

A stable product ($\lambda_{\text{max}} \approx 400$ nm) and transient bands in the blue (410 - 430 nm) and the red regions (a characteristic double band with maxima in the range 610 - 750 nm) were observed in all solvents. The two transient bands exhibit similar decay kinetics and are therefore assigned to the same transient species. The results obtained for MPI (Fig. 4) show comparable features; in this case, however, no transient absorption could be seen in cyclohexane, and no stable product was formed in alkaline water. The long wavelength band of the MPI transient is unstructured.

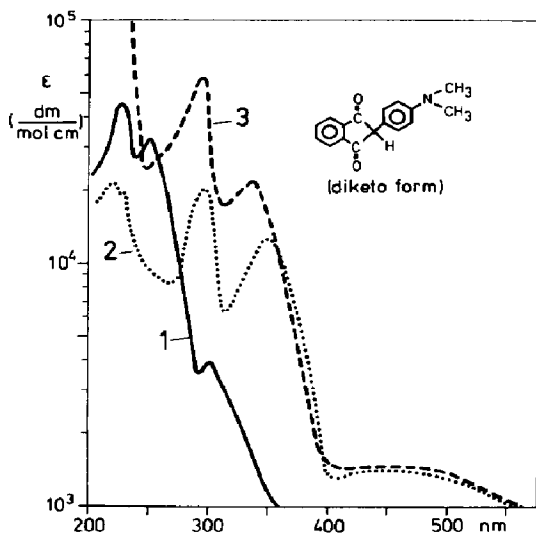


Fig. 1. Absorption spectra of DAPI in cyclohexane (curve 1), ethanol (curve 2) and water (pH 12) (curve 3).

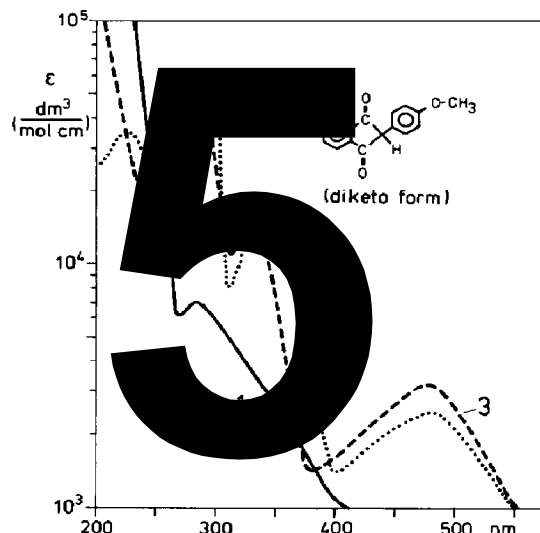


Fig. 2. Absorption spectra of MPI in cyclohexane (curve 1), ethanol (curve 2) and water (pH 12) (curve 3).

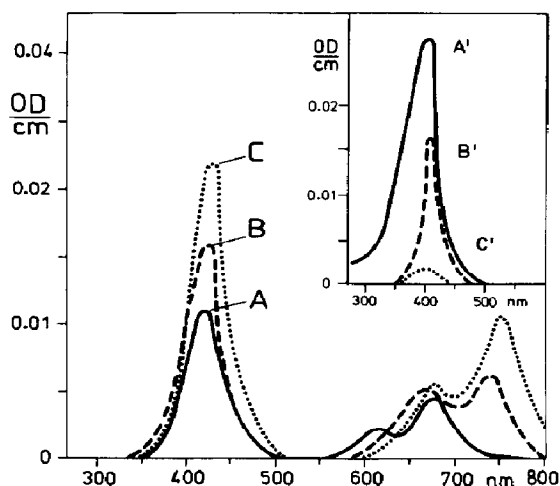


Fig. 3. Absorption spectra of transients formed by the flash photolysis of DAPI solutions of concentration $10^{-4} \text{ mol dm}^{-3}$, purged with argon (discharge voltage, 8 kV; 750 μs after flash): curve A, cyclohexane solvent; curve B, ethanol solvent; curve C, water (pH 12) solvent. The inset shows the absorption spectra of stable end products under the same conditions.

The absorption maxima of the stable products, which are formed in the submicrosecond range, agree well with those of the corresponding benzylidenephthalides (reaction (1)) [26]. The observed transients (see below) are too long lived to be their precursors.

TABLE 1

Absorption maxima of 2-(4'-dimethylaminophenyl)-indan-1,3-dion-2-yl radicals in various solvents

Solvent	Absorption maxima λ_{\max} (nm)	Applied method ^a	Reference ^b
Cyclohexane	420, 610, 670	A	This work
Ethanol	430, 660, 735	A	
Water (pH 12)	410, 670, 750	A	
Chlorobenzene	670, 730	B, C	[23]
Toluene	420, 650, 710	A, C	[24]
1,2-dichloroethane	735	C	[25]
Dimethylsulphoxide	735	C	[25]
Chloroform	745	C	[25]

^a A, flash photolysis of DAPI; B, flash photolysis of dimer; C, thermolysis of dimer.

^b The measurements reported in refs. 23 and 25 were confined to the long wavelength bands.

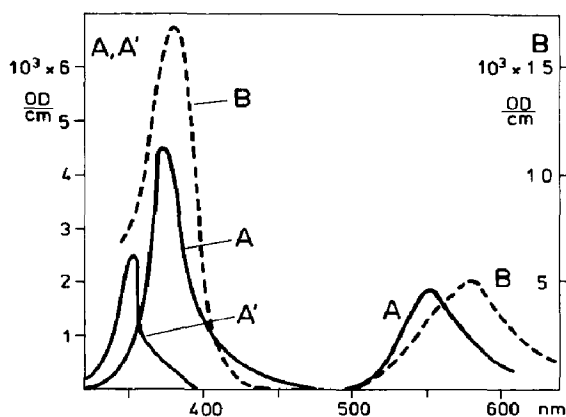


Fig. 4. Absorption spectra of transients formed by the flash photolysis of MPI solutions of concentration 2×10^{-5} mol dm⁻³ purged with argon (discharge voltage, 8 kV): curve A, ethanol solvent (100 μ s after the flash); curve A', ethanol solvent (30 s after the flash); curve B, alkaline aqueous solution (100 μ s after the flash).

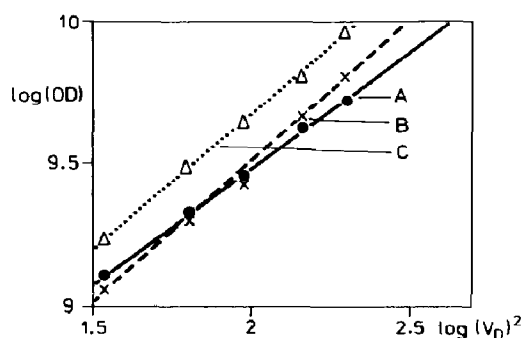


Fig. 5. Dependence of the yields of the flash photolysis of MPI in ethanol (5×10^{-5} mol dm⁻³; $\lambda = 370$ nm) on the square of the discharge voltage: curve A, in air (200 μ s after the flash); curve B, in air (stable product); curve C, in argon (200 μ s after the flash).

The transient band shapes are similar in all solvents investigated, but the spectral position of the long wavelength band is strongly affected by the solvent; polar solvents cause a bathochromic shift (Figs. 3 and 4 and Table 1).

The yields of both transients and stable products are proportional to the intensity of the photolysing flash (Fig. 5); this indicates that they are formed in monophotonic processes. Figure 5 also shows that the transient absorption is reduced in the presence of oxygen. The transients decay according to second-order kinetics; $k_2/\epsilon = 1.2 \times 10^5$ m s⁻¹ is obtained for DAPI radicals in ethanol at 735 nm. If an extinction coefficient ϵ of 8×10^4

$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, as observed for the long wavelength maximum at 730 nm in chlorobenzene [23], is assumed, a second-order rate constant k_2 of about $9.7 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$ can be evaluated.

It was further observed that the DAPI transient yields were lower in cyclohexane than in ethanol or alkaline water. However, this may be explained in part by the fact that, owing to its absorption spectrum, the diketo form absorbs only a small fraction of the total flash emission. More significant is the considerable increase in the relative yield of the transient compared with that of the product (benzylidenephthalide) in aqueous alkaline solution.

3.3. Determination of the benzylidenephthalide quantum yield from 2-(4'-methoxyphenyl)-indan-1,3-dione in ethanol

In contrast with the usually non-fluorescent indandiones, the benzylidenephthalides have a relatively high fluorescence quantum yield ($Q_F = 0.3$ for the methoxy derivative [26]). Fluorescence is therefore suitable for the determination of the photolytic product yields.

Air-free solutions of MPI in ethanol (concentration, $1.0 \times 10^{-4} \text{ mol dm}^{-3}$) were irradiated at various wavelengths. The fluorescence of the irradiated sample was compared with that of solutions with known concentrations of methoxybenzylidenephthalide. The initial product quantum yields at 220, 285 and 340 nm are compiled in Table 2 where it can be seen that they show a strong wavelength dependence.

TABLE 2

Quantum yields for the formation of benzylidenephthalide from the photolysis of solutions of 2-(4'-methoxyphenyl)-indan-1,3-dione in argon-saturated ethanol (concentration, $1.0 \times 10^{-4} \text{ mol dm}^{-3}$)

Product formation wavelength (nm)	Q (phthalide)
340	0.00009
285	0.0021
220	0.009

3.4. Electron photoejection from 2-(4'-methoxyphenyl)-indan-1,3-dione in alkaline water

At pH 12 the indandiones are present in the enolate form [9, 10]. The possibility of electron photoejection in these systems was tested on MPI using chloroacetate as a scavenger. The results are shown in Table 3.

Neither Cl^- formation nor substrate degradation were observed on irradiation at 330 nm, in contrast with the results obtained at 254 nm. The quantum yields for the two processes are of the same order of magnitude. Both yields increase on using higher scavenger concentrations. The sample absorption changes substantially on irradiation, the product extinction being

TABLE 3

Quantum yields of chloride and of degradation in the photolysis of aqueous alkaline solutions (pH 12) of 2-(4'-methoxyphenyl)-indan-1,3-dione (10^{-4} mol dm $^{-3}$) containing chloroacetate

λ_{exc} (nm)	UV dose (quanta ml $^{-1}$)	[ClCH $_2$ COO $^{-}$] (mol dm $^{-3}$)	Q (Cl $^{-}$)	Q (degradation)
330	3.1×10^{18}	0.002	$< 3 \times 10^{-4}$	$< 4 \times 10^{-4}$
254	1.9×10^{18}	0.002	0.0066	0.0071
254	1.9×10^{18}	0.005	0.0090	0.100

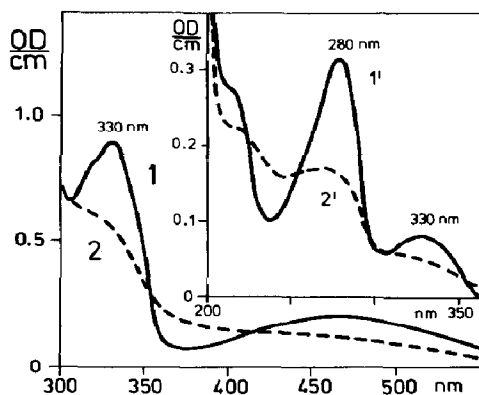


Fig. 6. UV absorption spectra of argon-purged MPI solutions in water (pH 12) (concentration, 10^{-4} mol dm $^{-3}$): curve 1, before irradiation; curve 2, after 10 min UV irradiation at $\lambda = 254$ nm (see text). The inset shows the UV absorption spectra of MPI solutions in water (pH 12) (concentration, 10^{-5} mol dm $^{-3}$): curve 1', before irradiation; curve 2', after 10 min UV irradiation at $\lambda = 254$ nm.

generally lower and shifted to shorter wavelengths (Fig. 6). The absorption above 350 nm is mainly due to the remaining substrate in the solution.

3.5. Pariser-Parr-Pople calculations

The π bond orders computed according to Coulson [27] for those atoms and bonds of the enol and enolate forms of 2-phenylindandione which are relevant to the present work are given in Table 4.

4. Discussion

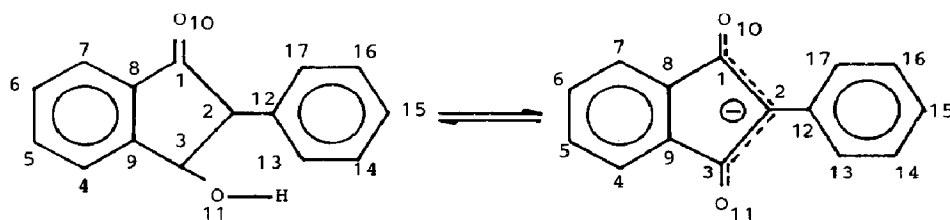
The results of the present work show that the flash photolysis of 2-phenylindandione derivatives results in the formation of both stable final products (the corresponding benzylidenephthalides) and transients, and that two independent photolytic pathways are operating.

The transient absorption spectrum of DAPI (Fig. 3) is in good agreement with that of the DAPI radical produced by photolysis [23, 28, 29] or

TABLE 4

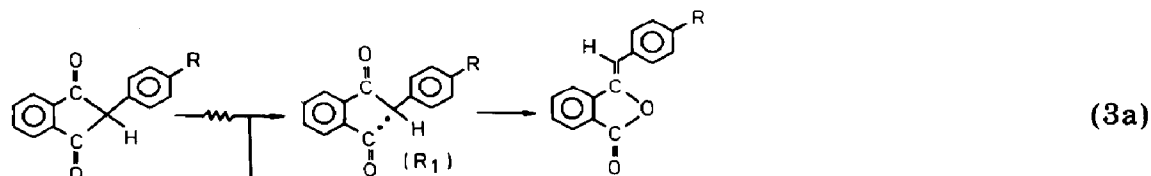
Selected π bond orders of the enol and enolate forms of 2-phenylindan-1,3-dione in various electronically excited states obtained by Pariser-Parr-Pople self-consistent field configuration interaction calculations

Bond	Bond order			
	S_0 state	S_1 state	S_2 state	T_1 state
<i>Enol form</i>				
1-2	0.311	0.375	0.365	0.458
2-3	0.828	0.495	0.735	0.333
2-12	0.201	0.294	0.214	0.250
1-8	0.286	0.434	0.386	0.351
3-9	0.288	0.512	0.408	0.458
<i>Enolate form</i>				
1-2 } 2-3 }	0.540	0.378	0.379	0.391
2-12				
1-8 } 3-9 }	0.203	0.425	0.266	0.391

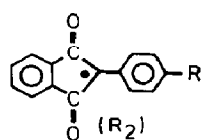


thermolysis [23, 24, 28, 29] of the dimer. The decay of the radical leads back to the dimer. It should be noted that the dimer can also be obtained by radical-mediated one-electron oxidation (e.g. with HNO_3 , $\text{K}_3[\text{Fe}(\text{CN})_6]$ or $\text{I}_2\text{-OH}^-$) [1, 30]. The assignment of the observed transient spectra to 2-arylidindan-1,3-dion-2-yl radicals therefore seems to be well established.

The spectroscopic and analytic data obtained enable the following primary photolytic processes to be assumed:



(3a)

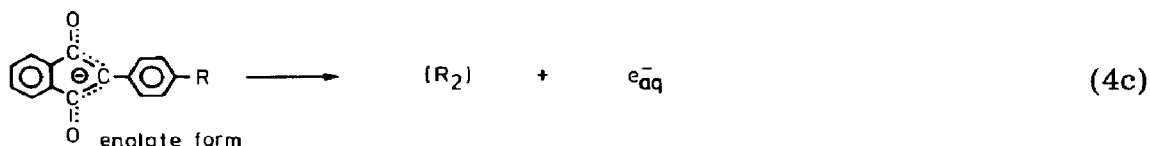
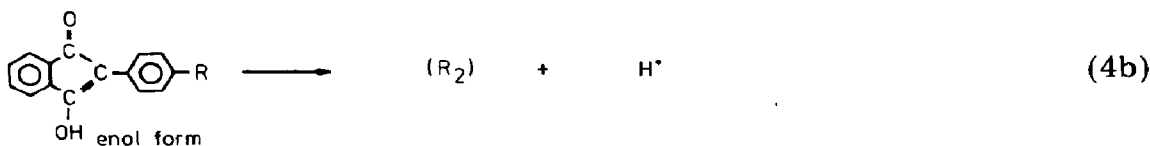
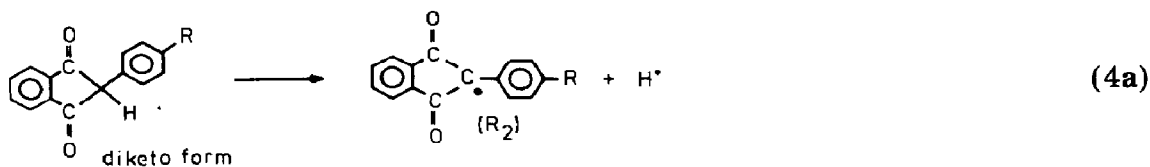


(3b)

The rearrangement of 2-arylidandiones to the corresponding benzylidenephthalides may also be effected by ground state protonation of the carbonyl group in strongly acidic medium by means of hydrobromic acid [31].

The radicals R_2 react according to second-order kinetics; this can be interpreted as a dimerization reaction. The dimer cannot tautomerize to the enol form because its structure consists of two uncoupled subchromophores (2-phthaldialdehyde) which are identical with the diketo chromophore. In agreement with this conclusion, the products of enolate photolysis absorb only in the far UV region (see Section 3.4).

Photocleavage at the α position (reaction 3(b)) leads to radical R_2 . Analogous processes have also been encountered with other keto compounds [32, 33]. It is interesting to note that the same radical can be obtained with higher yields from the enol form by splitting the OH bond or via electron photoejection from the enolate form. Evidence for this last process has been obtained from the scavenger experiments described in Section 3.4. The three pathways of R_2 formation are summarized below and can be classified as photo-oxidation reactions:



No information is available about the spectroscopic and kinetic properties of the hypothetical biradical R_1 resulting from C1—C2 cleavage (Norrish type I mechanism) which is the precursor of the benzylidenephthalides. This is not unexpected since it should be very short lived, one rotation about a C—C single bond being sufficient to accomplish the rearrangement. Preliminary results obtained by means of time-resolved fluorescence measurements (PRA system 2000, Canada) give strong evidence for subnanosecond formation of phthalide.

The isomerization to phthalides is achieved with much higher yields from the diketo form (Fig. 3); this is of particular importance in preparative applications. Nevertheless, as this work shows for the first time, phthalide formation is also possible from the enol and enolate forms.

The higher phthalide yields from the diketo form are expected in view of the PPP-SCF-CI calculations (Table 4). In this form atom 2 is in sp^3 hybridization and bonds 1-2 and 2-3 are typical single bonds. In contrast, pronounced double-bond character prevails in the enol and enolate forms for bond 2-3 (π bond orders of 0.83 and 0.67 respectively). These values are somewhat lower in the singlet and triplet excited states, but remain greater than zero. Both the 1-2 and 2-3 bonds are stronger than typical single bonds in the excited states.

Apart from the possible contributions of the S_1 and T_1 states to the observed photochemical processes, higher excited singlet states may also play an important part. This is shown by the considerable wavelength dependence of the quantum yields of both phthalide and e_{aq}^- . No evidence for biphotonic processes via the lowest triplet state was obtained in the flash photolysis experiments.

Acknowledgments

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