Steady-State and Flash Photolysis Investigations of 1 H-Indene-1,3 (2 H)-Dione Derivatives

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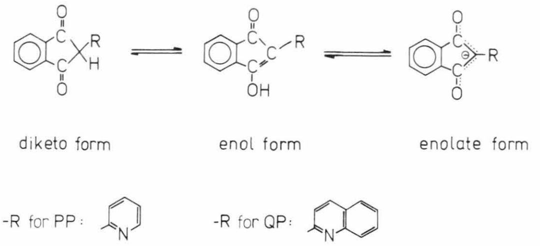
Pyrophthalone (PP, 2-(2-pyridinyl)-1 H-indene-1,3 (2 H)-dione) and quinophthalone (QP, 2-(2-quinolinyl)-1 H-indene-1,3 (2 H)-dione) were investigated in various solvents with respect to their photostability. It was found that PP and QP in ethanol as well as QP in cyclohexane are rather stable under steady-state conditions using UV light ($\lambda = 253.7$ nm). Conventional as well as laser flash photolysis of airfree aqueous alkaline solutions (pH 12) lead to the formation of different radicals and solvated electrons (e_{aq}^-). Some reaction rates were determined and probable reaction mechanisms were postulated.

Key words: Pyrophthalone (PP), Quinophthalone (QP), Flash photolysis, Transient absorption spectra, Steady state photolysis.

1. Introduction

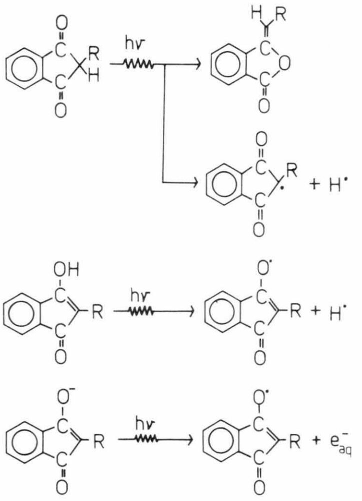
Pyrophthalone (PP, 2-(2-pyridinyl)-1 H-indene-1,3-(2 H)-dione), quinophthalone (QP, 2-(2-quinolinyl)-1 H-indene-1,3 (2 H)-dione) and other derivatives of 1 H-indene-1,3 (2 H)-dione are used as dyes [1, 2] and anti-inflammatory and anaesthetic agents [3, 4]. Furthermore, they can act as organic semiconductors [5] and complexing agents [5–7].

In solutions, depending upon solvent polarity and pH, some of the derivatives can exist in three forms: diketo, enol and enolate form:



(1)

In the case of derivatives investigated during previous studies (especially R = substituted phenyl), in apolar solvents (cyclohexane) the molecules are present in the β-diketone structure, while in polar solvents (alcohols, water) the enol structure is formed [8]. In alkaline aqueous solutions the equilibrium is shifted to the enolate form. The photochemistry of this group of substances in solution has been characterised by the mechanisms shown in reactions (2)–(4).



(2a)

(2b)

(3)

(4)

Neutral radicals can be formed by splitting the H atom (in α-postition to both carbonyl groups or in the OH group) from neutral excited molecules, or by electron ejection from the enolate form [8], (4). The kinetics of dimer formation from these radicals has been previously investigated [9, 10]. In addition, photoisomerisation in apolar solvents leading to the corresponding 3-phenylmethylene-1 (3 H)-isobenzofuranones

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(benzylidenephthalides) has been also observed, most likely occurring after bond splitting due to a "Norrish type I" mechanism [8, 11–16].

Based on previous studies on 2-phenylindan-1,3-dione derivatives in polar and apolar solvents [8, 17] it is expected that in the case of PP and QP the diketo structure will be unstable, even in apolar solvents; further, that inter- and intramolecular hydrogen bonds of the enol form will predominate.

The aim of the present investigations was, therefore, to examine the expectations resulting from experiments with other derivatives, e.g. [8, 9, 11, 18–20]. In addition to this it was of interest to get a detailed insight into the photochemistry of PP and QP and, especially, into the formation of different photochemical transients induced by conventional and laser flash photolysis.

2. Experimental

Preparation of Solutions

The investigated substrates were synthetized according to standard procedures (e.g. [21], and references therein). After several recrystallisations their purity was checked by thin-layer chromatography. All other chemicals (E. Merck, Darmstadt) were p.a. quality. The water used for preparation of solutions was triply distilled. The absorption spectra were measured with a double-beam spectrophotometer (Hitachi, model 150-20).

UV-Irradiation

Steady-state photochemical experiments were performed in a 4π-irradiation setup [22] using a low-pressure Hg-lamp (Osram HNS 10 ofr with incorporated filter for the 184.9 nm line), which emits light with $\lambda = 253.7$ nm only. All irradiations were carried out at 30 ± 1 °C. The solutions were purged with high purity argon in order to remove the oxygen before irradiation. Actinometry with airfree 0.5 mol dm^{-3} chloroacetic acid ($Q_{\mathrm{Cl}^-} = 0.34$ at 30 °C) [23, 24] yielded a light intensity of $I_0 = 5 \times 10^{17}$ quanta ml^{-1} min^{-1}.

The formation of solvated electrons (e_{aq}^-) in aqueous alkaline solutions (pH 12) was measured by using chloroacetate as electron scavenger:

$$\mathrm{ClCH_2COO^-} + e_{aq}^- \rightarrow \mathrm{Cl^-} + \dot{\mathrm{C}}\mathrm{H_2COO^-}, \quad (5)$$

$$k = 1.0 \times 10^9\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [25].$$

The $\mathrm{Cl^-}$ yield was determined spectrophotometrically [26].

Conventional Flash Photolysis

The transient absorption spectra resulting from PP and QP were obtained by means of a conventional flash photolysis apparatus (Northern Precision, modified: air-filled flash lamp, flash duration 7 µs with variable energy of 20–200 J) described earlier [27]. The detection of each individual signal was now improved by a Philips digital storage oscilloscope (PM 3320/40) in connection with a Sharp PC-4500. This set-up allows a repetitive sampling procedure and hence an increase of the measurement accuracy.

Laser Flash Photolysis

A frequency-quadrupled, Q-switched Nd:YAG laser (Quanta-Ray DCR-1), emitting at $\lambda = 266$ nm with a pulse duration of 10 ns was used for excitation of aqueous PP at pH 12 in laser flash photolysis measurements. Details of the experimental setup and procedures have been published [28, 29].

3. Results and Discussion

3.1. Absorption Spectra

The absorption spectra of pyrophthalone (PP) and quinophthalone (QP) in different solvents (cyclohexane, neutral and alkaline aqueous solutions) are presented in Figs. 1 and 2. The spectra show clearly that in aqueous solution at pH 12 both, PP and QP, are deprotonated and form enolate anions like other derivatives of 1 H-indene-1,3(2 H)-dione, cf. (1). A difference between aqueous and cyclohexane solutions was also observed, indicating the presence of different forms of the substrate.

3.2. Steady-State Photolysis

For determination of the photoinduced decomposition quantum yields, Q(-substrate), 2×10^{-4} mol dm^{-3} PP or QP in ethanol were used. The solutions were irradiated with UV-light of $\lambda = 253.7$ nm. Under these conditions the Q(-substrate) obtained was 7×10^{-5} for PP and 4×10^{-5} for QP. One additional experiment was performed with 10^{-4} mol dm^{-3} QP in cyclohexane. In this case also the decomposition quantum yield was low, Q(-substrate) $< 10^{-4}$.

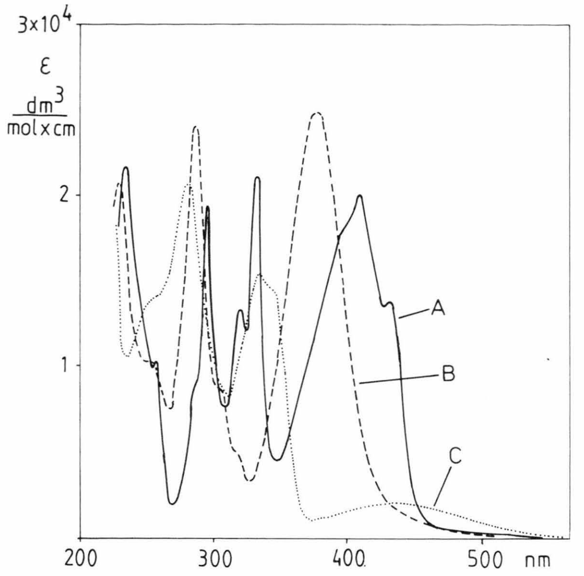

Fig. 1. Absorption spectra of 10^{-5} mol dm^{-3} PP in different solvents. A, cyclohexane; B, neutral aqueous solution; C, alkaline aqueous solution (pH 12).

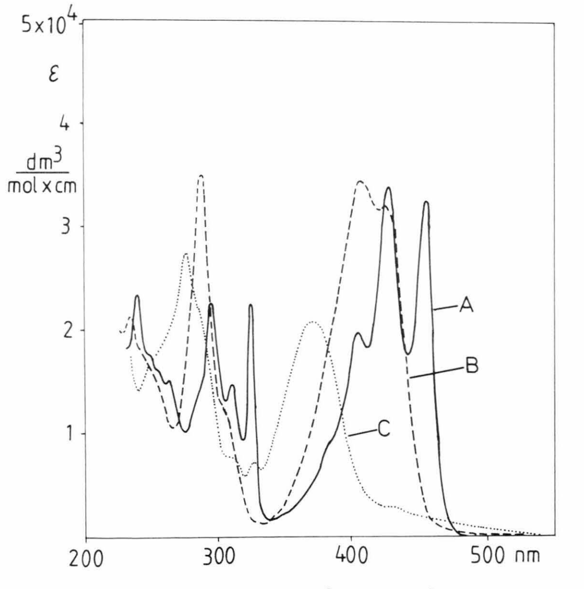

Fig. 2. Absorption spectra of 10^{-5} mol dm^{-3} QP in different solvents. A, cyclohexane; B, neutral aqueous solution; C, alkaline aqueous solution (pH 12).

The quantum yields obtained for formation of solvated electrons in aqueous alkaline solutions (pH 12) are:

for PP: $Q(e_{aq}^-) = 0.006$ and

for QP: $Q(e_{aq}^-) = 0.009$.

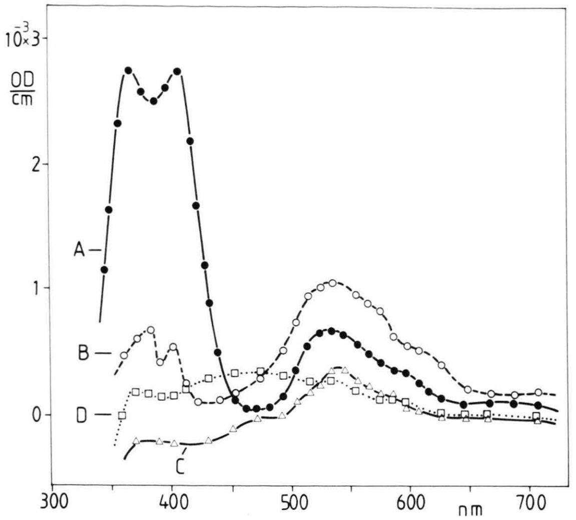

Fig. 3. Transient spectra obtained by conventional flash photolysis of 10^{-5} mol dm^{-3} alkaline aqueous solution of PP (pH 12). A, argon-saturated; B, 2.8×10^{-2} mol dm^{-3} N_2O; C, 2.8×10^{-2} mol dm^{-3} N_2O + 0.1 mol dm^{-3} tert. butanol; D, 1.25×10^{-3} mol dm^{-3} O_2.

3.3. Conventional Flash Photolysis Experiments

The transient absorption spectra resulting from both PP and QP were observed under various experimental conditions using the conventional flash photolysis technique. The most interesting results were obtained in alkaline aqueous solutions (pH 12) using 10^{-5} mol dm^{-3} substrate. They were saturated with argon or with N_2O, and in some cases with air or oxygen. A second series of experiments was performed in the presence of N_2O after addition of 0.1 mol dm^{-3} t-butanol acting as OH-scavenger:

$$OH^{\cdot} + \text{t-}C_4H_9OH \rightarrow \text{t-}\dot{C}_4H_8OH + H_2O, \qquad (6)$$

$$k = 5.5 \times 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ [30].$$

Transients Resulting from Pyrophthalone

The transient absorption spectra obtained by using 10^{-5} mol dm^{-3} PP under different experimental conditions are shown in Figure 3.

In solutions saturated with argon the observed spectrum A, Fig. 3 (λ_{max} at 365, 405 and 535 nm) consists of several transients formed according to reactions (2) to (4). At pH = 12, however, reaction (4) is the most probable one. Furthermore, the photoejected e_{aq}^- can react with the substrate leading to the formation of the corresponding transient:

$$\mathrm{PP} + e^-_{aq} \rightarrow \mathrm{PP}^{\cdot -} \text{ (electron adduct)}. \quad (7)$$

By scavenging e^-_{aq} with N_2O,

$$e^-_{aq} + N_2O \rightarrow N_2 + OH^- + OH^{\cdot}, \quad (8)$$

$$k = 0.91 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}\ [31],$$

absorption spectrum B, Fig. 3, is obtained. The maxima at 365 and 405 nm are strongly reduced, but at the same time the absorption band at 535 nm is increased (see spectra A and B). Hence, it can be concluded that the absorption maxima at 365 and 405 nm and partly at 535 nm belong to the $\mathrm{PP}^{\cdot -}$ species. The OH-radicals produced by reaction (8) lead to the formation of the OH-adduct ($\mathrm{P\dot{P}-OH}$), which is represented by the absorption band at 535 nm, spectrum B.

$$\mathrm{PP} + OH^{\cdot} \rightarrow \mathrm{PPOH}^{\cdot} \text{ (OH adduct)}. \quad (9)$$

When both, e^-_{aq} and $\dot{O}H$, are removed, a further strong change of the spectrum is observed (spectrum C, Figure 3). The resulting spectrum shows an absorption band at 550 nm, probably representing the radical $\mathrm{PP}^{\cdot}$ originating from reaction (4).

In the presence of oxygen the formation of $O_2^{\cdot -}$ radicals occurs, which can react with the substrate:

$$e^-_{aq} + O_2 \rightarrow O_2^{\cdot -}, \quad (10)$$

$$k = 1.9 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}},\ [32],$$

$$\mathrm{PP} + O_2^{\cdot -} \rightarrow \mathrm{PP{-}O_2^{\cdot -}} \text{ (peroxy-adduct)}. \quad (11)$$

On the other hand it is also known that oxygen is able to react with radical species (here $\mathrm{PP}^{\cdot}$) under formation of the corresponding peroxy-radicals:

$$\mathrm{PP}^{\cdot} + O_2 \rightarrow \mathrm{PP{-}O{-}O}^{\cdot}. \quad (12)$$

Spectrum D, Fig. 3, observed under these conditions possesses a weak broad absorption band from 450 to 550 nm. This transient may be attributed to species formed in reaction (11) or (12).

Transients Resulting from Quinophthalone

In analogy to PP, similar flash photolysis experiments were performed with 10^{-5} mol dm^{-3} QP in alkaline aqueous solution (pH 12). The observed transient absorption spectra are presented in Figure 4.

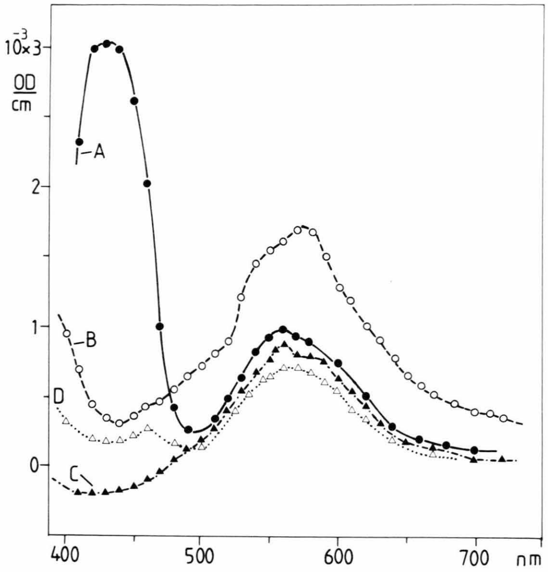

Fig. 4. Transient spectra obtained by conventional flash photolysis of 10^{-5} mol dm^{-3} alkaline aqueous solution of QP (pH 12). A, argon-saturated; B, 2.8×10^{-2} mol dm^{-3} N_2O; C, 2.8×10^{-2} mol dm^{-3} $N_2O + 0.1$ mol dm^{-3} tert. butanol; D, 1.25×10^{-3} mol dm^{-3} O_2.

In solutions saturated with argon a characteristic spectrum A, having two strongly pronounced maxima at 430 and 560 nm, is obtained. In the presence of 2.8×10^{-2} mol dm^{-3} N_2O the absorption band at 430 nm is diminished, whereas the absorption around 570 nm is strongly increased. This is the same effect as described above for PP (Figure 3). Hence, the absorption band at 430 nm and partly that in the range of 500 to 650 nm is assigned to the electron adduct of the substrate ($\mathrm{QP}^{\cdot -}$).

The OH radicals appearing as a product of reaction (8) lead to the formation of the corresponding OH-adduct ($\mathrm{QP{-}OH}^{\cdot}$, spectrum B) with a major absorption maximum at 570 nm. By removing both species, e^-_{aq} and $OH^{\cdot}$, spectrum C is observed with an absorption maximum at 560 nm and a shoulder at about 580 nm. As in the case of PP, this absorption is attributed to the radicals $\mathrm{QP}^{\cdot}$ produced by electron ejection (see reaction (4)). Spectrum D, measured in the presence of oxygen, shows an absorption maximum at 570 nm.

Comparing the spectra resulting from PP and those of QP observed under the same experimental conditions using QP, the great similarity between them is obvious.

Table 1. Decay half time (τ, μs) of transients originated from 10^{-5} mol dm^{-3} pyrophthalone (PP) and quinophthalone (QP) in alkaline aqueous solution (pH 12), saturated with argon, N_2O, N_2O in the presence of 0.1 mol dm^{-3} t-BuOH and with oxygen.

Experimental conditions	Transients originating from			
	PP		QP	
	λ (nm)	τ (μs)	λ (nm)	τ (μs)
Airfree	380 530	290 590	440 560	260 390
N_2O	530	1100	570	690
N_2O/t-BuOH	530	480	565	680
Oxygen	–	–	570	730

Kinetics

Based on the spectral data discussed above it is obvious that the major process in alkaline aqueous solution is electron ejection, reaction (4). In all cases the decay of the species at the beginning followed a first order reaction. Hence, it was possible to evaluate the half life time (τ, μs) of the transients at the absorption maxima. They are presented in Table 1.

3.4. Laser Flash Photolysis of Pyrophthalone

Pyrophthalone triplet formation. The quantum yield of intersystem crossing of pyrophthalone (PP) in ethanol has been measured by means of energy transfer to anthracene [33]. In a solution containing 9.3×10^{-5} mol dm^{-3} anthracene and 1.43×10^{-4} mol dm^{-3} PP, no formation of anthracene triplets by energy transfer from excited PP could be detected. Ths indicates that intersystem crossing in pyrophthalone is negligible.

Hydrated electron formation. In an aqueous 2×10^{-5} mol dm^{-3} PP solution (pH 12) saturated with argon the formation of e_{aq}^- was detected by its absorption at $\lambda_{max} = 720$ nm. Assignment to e_{aq}^- is confirmed by quenching of its absorption in N_2O-saturated solution and reaction with O_2 (reactions (8) and (10)).

Figure 5 shows dependence of the optical density (OD) due to e_{aq}^- at $\lambda = 650$ nm on laser pulse energy. A strongly non-linear behaviour, indicative of important two-photon contribution to electron ejection, is obtained. Analysis for superposition of one- and two-photon processes is accomplished by means of the relation [29]

$$OD_{650} = a \times P + b \times P^2 , \qquad (13)$$

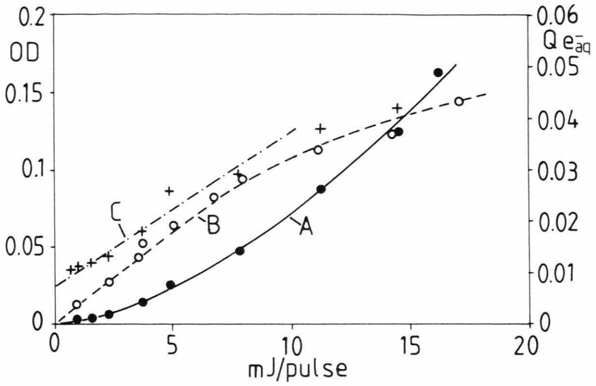

Fig. 5. Dependence of laser-induced transient absorbance and of e_{aq}^- quantum yield on pulse energy (2×10^{-5} mol dm^{-3} PP, solution saturated with argon, pH 12). (A) Absorbance at pulse end, $\lambda = 650$ nm. (B) Absorbance after completion of build-up, $\lambda = 390$ nm, values multiplied by factor 10. (C) e_{aq}^- quantum yields as obtained from analysis according to (13).

where OD_{650} is e_{aq}^- absorbance at 650 nm, P is the laser pulse energy and a and b are parameters depending on the molar extinction coefficients of the involved transitions, the quantum efficiencies of the individual steps and on irradiation geometry. Since the molar extinction coefficient of e_{aq}^- at 650 nm is known ($\varepsilon_{650} = 16260$ dm^3 mol^{-1} cm^{-1} [34]), the quantum yield ($Q(e_{aq}^-)$ relative to absorption of 266 nm photons by ground-state pyrophthalone can be determined. This is shown in Figure 5. A linear dependence between $Q(e_{aq}^-)$ and P is obtained up to 10 mJ/pulse, showing the predominance of two-photon processes. A small positive y-axis intercept is, however, also obtained from which a quantum yield for one-photon electron ejection of 0.007 can be determined, in excellent agreement with the result of the steady-state scavenger experiment.

Decay of e_{aq}^- is predominantly by a second-order reaction. At the lowest pulse energy used, decay halftime is about 1 μs.

Transient spectra and kinetics. Fig. 6 shows the spectra of laser-induced transients obtained at 12 mJ/pulse in aqueous solutions of pyrophthalone at pH 12. In argon-saturated solution an increase of absorption after the pulse is noticed, which correlates in time with e_{aq}^- decay. This build-up is absent in presence of N_2O. In argon-saturated solution the transient spectrum, measured 1 μs after pulse end, i.e. after completion of the build-up at 12 mJ/pulse, shows maxima at 300 nm and 370 nm and minima at 270 nm and 340 nm, the

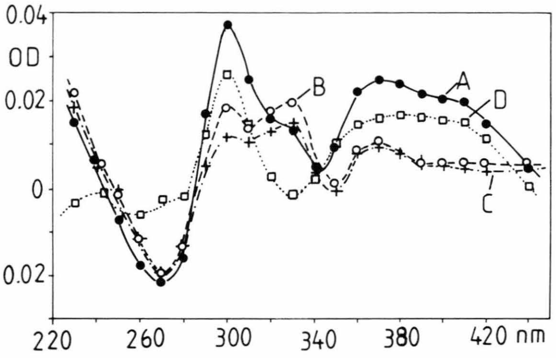

Fig. 6. Uncorrected transient absorption spectra from laser flash photolysis (12 mJ/pulse) of 4×10^{-5} mol dm^{-3} PP in aqueous solution. (A) Solution saturated with argon, absorbance measured 1 µs after the end of pulse. (B) Solution saturated with N_2O, 0.1 mol dm^{-3} t-butanol added, absorbance measured at pulse end. (C) Solution saturated with N_2O, 0.1 mol dm^{-3} t-butanol added, absorbance measured 1 µs after end of pulse. (D) Difference between (A) and (C).

latter coinciding with the absorption bands of pyrophthalone. These minima are, therefore, due to ground-state depletion. In solutions saturated with N_2O (2.8×10^{-2} mol dm^{-3}) the end-of-pulse spectrum shows a maximum at 330 nm. Absorption of the 370 nm band is strongly reduced as compared to the argon-saturated solution. End-of-pulse absorption is in this case difficult to measure; it appears to be comparable to that obtained in presence of N_2O. Figure 6 shows also the difference between spectra in argon and N_2O taken 1 µs after the pulse; two bands appear in this spectrum with $\lambda_{max} = 300$ nm and 390 nm.

Decay kinetics of the 330 nm band in presence of N_2O is of second order with $2k/\varepsilon = 1 \times 10^7$ cm s^{-1}.

Assignment of the spectra shown in Fig. 6 is straightforward. Build-up of absorption after the exciting pulse in argon-saturated solution demonstrates formation of radical anions $PP^{\cdot -}$ by reaction (7). Spectrum D in Fig. 6 is assigned to this species; the broad band with $\lambda_{max} = 390$ nm is to be compared with spectrum A in Figure 3. The local minimum at $\lambda = 380$ nm may be absent in Fig. 6 because of the uncertainty in the determination of the difference spectrum. In N_2O-saturated solution containing tert. butanol, only the radicals produced by reaction (4) should contribute. They are characterised by a peak at $\lambda = 330$ nm (spectrum B in Fig. 6), decaying in a second-order reaction as mentioned above; this may be explained by the higher transient concentration produced in laser as compared to conventional flash photolysis.

Dependence of OD at 390 nm after completion of build-up in argon-saturated solution is shown in Figure 5. The functional dependence is in this case different from that obtained for the absorption at 650 nm (e_{aq}^-). This can be explained by the fact that with increasing pulse energy the proportion of e_{aq}^- reacting with pyrophthalone is decreasing due to competition from second-order reaction of e_{aq}^-.

4. Conclusion

Pyrophthalone (PP) and quinophthalone (QP) were investigated with respect to their photostability and transient formation in alkaline aqueous solution. Their high photostability in cyclohexane as well as in ethanol can be explained by the high stability of the enol form, resulting from hydrogen linkages and mesomeric effects caused by the heterocyclic nitrogen atom. As a consequence, there is no formation of isomerisation products as observed with other derivatives with nitrogen-free substituents. Furthermore, on excitation of PP and QP in alkaline aqueous solution by different flash photolysis methods, in addition to the formation of solvated electrons (e_{aq}^-) and the radicals $PP^{\cdot}$ and $QP^{\cdot}$, reaction (4), also the electron adducts, OH-adducts and peroxy-radicals could be observed. The greater part of these radicals are formed by two-photon processes in the conditions of laser excitation. The same may be true in conventional flash photolysis experiments. A small quantum yield for one-photon electron ejection (<0.01) was determined by scavenger as well as by laser flash methods. Since radical formation results from electron ejection, their yield will be relatively low in steady state conditions, in accordance with the high photostability of the substances.

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[1] B. K. Manukian and A. Mangiani, Chimia **24,** 382 (1970).

[2] M. Tomarek-Kunitzer, F.R.D.-Patent 1968, No. 1265582.

[3] J. Ploquin,. L. Sparfel, G. le Bant, L. Welin, I. Y. Petit, and N. Henry, Chim. Ther. **1973,** 350.

[4] G. le Bant, L. Sparfel, J. Ploquin, I. Y. Petit, N. Henry, and L. Welin, Bull. Soc. Pharm. de l'Quest **15,** 43 (1973).

[5] I. J. Neiland and J. J. Katzen, Khim. Geterozikl. Soed. **1975,** 435.

[6] R. Cook and D. F. Martin, J. Inorg. Nucl. Chem. **26,** 571 (1964).

[7] P. R. Bontchev, M. Mitewa, S. Minchev, M. Kashchieva, and D. Mechandjiev, J. Prakt. Chem. **325,** 803 (1983).

[8] J. Zechner, G. Grabner, G. Köhler, N. Getoff, I. Timtcheva, F. Fratev, and St. Minchev, J. Photochem. **23,** 61 (1983).

[9] I. V. Khudyakov, A. I. Yasmenko, and V. A. Kuzmin, Int. J. Chem. Kinet. **11,** 621 (1979).

[10] A. I. Yasmenko, I. V. Khudyakov, A. P. Darmanjan, V. A. Kuzmin, and S. Claesson, Chem. Scripta **18,** 49 (1981).

[11] J. Zechner, N. Getoff, I. Timtcheva, F. Fratev, and St. Minchev, Z. Naturforsch. **38a,** 1337 (1983).

[12] J. Rigaudy and P. Derible, Bull. Soc. Chim. Fr. **1965,** 3047.

[13] J. Rigaudy and P. Derible, Bull. Soc. Chim. Fr. **1965,** 3055.

[14] J. Rigaudy and P. Derible, Bull. Soc. Chim Fr. **1965,** 3061.

[15] A. Schönberg, G. O. Schenck, and O. A. Neumüller, Preparative Organic Photochemistry, Springer, Berlin **1968,** 43.

[16] I. Timtcheva, J. Zechner, N. Getoff, and St. Minchev, Z. Naturforsch. **40a,** 1040 (1985).

[17] B. K. Manukian and A. Mangini, Chimia **24,** 328 (1970).

[18] J. Zechner, N. Getoff, I. Timtcheva, F. Fratev, and St. Minchev, J. Mol. Structure **114,** 283 (1984).

[19] A. I. Yasmenko, A. A. Kuznetsov, and I. V. Khudyakov, Zh. Fiz. Khim. **54,** 1776 (1980).

[20] A. I. Yasmenko, A. P. Khardin, I. V. Khudyakov, and V. A. Kuzmin, Izv. Akad. Nauk. SSSR, Ser. Khim. **9,** 2014 (1980).

[21] I. Timtcheva, P. Nikolov, J. Zechner, N. Getoff, and St. Minchev, Z. Naturforsch. **42a,** 490 (1987).

[22] N. Getoff and G. O. Schenck, Photochem. Photobiol. **8,** 167 (1968).

[23] R. N. Smith, P. A. Leighton, and W. G. Leighton, J. Amer. Chem. Soc. **61,** 2299 (1939).

[24] M. Neumann-Spallart and N. Getoff, Radiat. Phys. Chem. **13,** 101 (1979).

[25] G. V. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, J. Phys. Chem. Ref. Data **17** (2), 513–886 (1988).

[26] T. M. Florence and Y. J. Farrar, Anal. Chim. Acta **54,** 373 (1971).

[27] G. Grabner, G. Köhler, J. Zechner, and N. Getoff, Photochem. Photobiol. **26,** 449 (1977).

[28] G. Grabner, G. Köhler, G. Marconi, S. Monti, and E. Venuti, J. Phys. Chem. **94,** 3609 (1990).

[29] G. Grabner, N. Getoff, Ts. Gantchev, D. Angelov, and M. Shopova, Photochem. Photobiol., in press.

[30] M. Gohn and N. Getoff, J. Chem. Soc., Faraday Trans. I, **73,** 1207 (1977).

[31] E. Janata and R. H. Schuler, J. Phys. Chem. **85,** 192 (1981).

[32] E. J. Hart and E. M. Fielden, Adv. Chem. Ser. **50,** 253 (1965).

[33] R. Klein, I. Tatischeff, M. Bazin, and R. Santus, J. Phys. Chem. **85,** 670 (1981).

[34] F. Y. Jou and G. Freeman, J. Phys. Chem. **83,** 2383 (1979).