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Photolabile surfactants based on the diazosulphonate group
2. 4-(Acyloxy)benzenediazosulphonates and 4-(acylamino)benzenediazosulphonates

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Abstract

The synthesis and characterization of photolabile surfactants, based on the light-sensitive diazosulphonate group, are described. The hydrophobic alkyl chain of these surfactants is connected by ester or amide bonding to the phenyldiazosulphonate moiety. The type of bonding has an influence on the Krafft temperatures, thermolability and photolability of the diazosulphonate surfactants. Photolysis proceeds via the corresponding diazonium salt by elimination of a sulphite ion from the diazosulphonate group. Thermolysis experiments were carried out in water (observed by UV spectroscopy) and in the solid phase (monitored by differential scanning calorimetry (DSC)).

Keywords: Photolabile surfactants; Diazosulphonate group

1. Introduction

In a recent paper [1], we reported the synthesis of new photodegradable surfactants based on the photolabile diazosulphonate group (4-*n*-alkylbenzenediazosulphonates). The hydrophobic part consists of an alkyl chain, connected directly to the aromatic part, while the hydrophilic moiety is composed of the light-sensitive diazosulphonate group. In this study (and a further paper), we describe the synthesis and characterization of other diazosulphonate surfactants, which differ in the kind of bonding of the alkyl chain to the aromatic part. The type of connection influences both the surfactant properties (Krafft temperatures) and the light sensitivity (due to electrical effects). This dependence is examined in detail. In this paper, we report the results obtained for surfactants in which the connecting group consists of ester or amide bonding.

2. Results and discussion

2.1. Synthesis of the diazosulphonate compounds

The diazosulphonates were prepared as displayed in Figs. 1 and 2. For the synthesis of the 4-(acyloxy)benzenediazosulphonates (Fig. 1), 4-aminophenol hydrochloride was diazotized by standard procedures and coupled with sulphite to yield 4-hydroxybenzenediazosulphonate. The latter product was acylated to the corresponding esters by the reaction with carboxylic

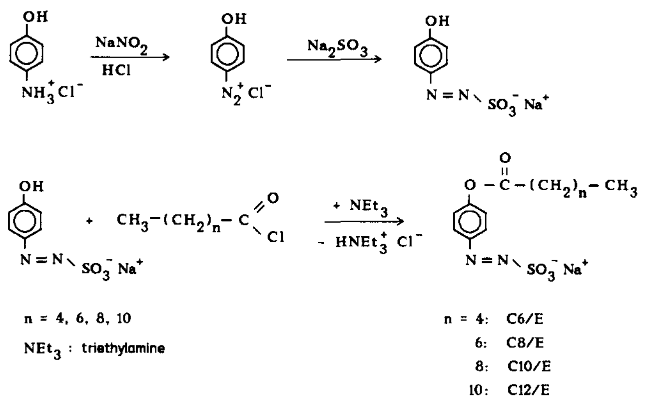

Fig. 1. Synthesis of sodium 4-(acyloxy)benzenediazosulphonates.

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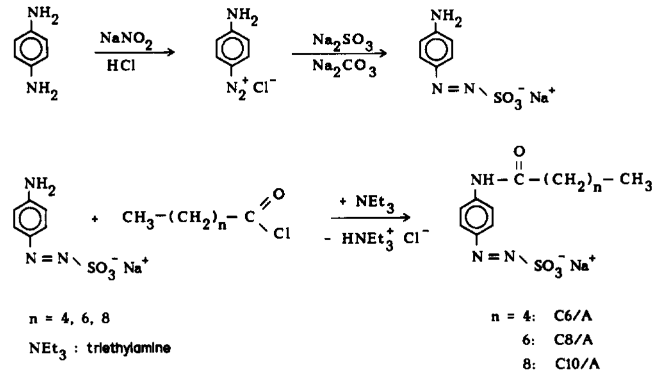

Fig. 2. Synthesis of sodium 4-(acylamino)benzenediazosulphonates.

acid chlorides of different chain lengths. Synthesis of the 4-(acylamino)benzenediazosulphonates (Fig. 2) follows the same strategy, with *p*-phenylenediamine instead of 4-aminophenol hydrochloride as starting compound.

The abbreviations for the synthesized diazosulphonate compounds (see Figs. 1 and 2) were chosen according to the number of carbon atoms in the alkyl chain and the kind of linkage of the alkyl chain to the aromatic part (E for ester and A for amide).

2.2. Critical micelle concentration (CMC) measurements

An important feature of a surfactant in water is the formation of micelles above a specific concentration (CMC) and a sufficiently high temperature, which is generally known as the Krafft temperature. In the case of diazosulphonate surfactants, the ability to form micelles has been demonstrated for 4-*n*-alkylbenzenediazosulphonate surfactants [1]. For the present class of compounds, precise CMC determinations are difficult in view of the thermolability of the diazosulphonate surfactants at elevated temperature.

To compare CMC values within a certain class of surfactants (in our case the synthesized "esters" or "amides"), CMC measurements should be performed at a temperature above the Krafft temperature of the surfactant with the longest hydrophobic part (C12/E or C10/A). Because of either high Krafft temperatures ("amides"; see Section 2.3) and/or high thermolability ("esters"; see Section 2.5), CMC measurements have not been carried out.

2.3. Krafft temperatures

The Krafft temperatures of the surfactants in water were regarded as the temperature at which a 1 wt.% suspension of the diazosulphonate surfactants cleared completely on gradual heating, as described in Ref. [1]. The results of these measurements are summarized in Table 1. As expected, the Krafft temperatures increase with increasing chain length, covering the range 47.5–71.5 °C in the case of the "esters". Contrary to the long-tailed compounds, no Krafft temperature could be determined for the compounds C6/E and C6/A, as the solubility is higher than 1 wt.% (a 1 wt.% solution was stored for 24 h at 4 °C, but no recrystallization was observed during this period). Presumably these compounds are not surfactants due to their short alkyl chain. In the case of C10/A, the diazosulphonate is so insoluble that a 1 wt.% solution could not be prepared even at the boiling point of water.

Table 1
Krafft temperatures of diazosulphonate surfactants

Compound	T_{Krafft} (°C)	Compound	T_{Krafft} (°C)
C6/E	–	C6/A	–
C8/E	47.5	C8/A	87.5
C10/E	59.5	C10/A	–
C12/E	71.5		

Table 2
UV data for the diazosulphonate compounds in distilled water. For the absorption coefficient ϵ, the mean value of all members of a class is given

Diazosulphonate	$\lambda_{\max}$ (nm)	ϵ (l mol^{-1} cm^{-1})
C6/E, C8/E, C10/E, C12/E	293.5	14200±300
C6/A, C8/A, C10/A	331.5	18200±200

2.4. Photolysis

Photolysis of the diazosulphonates was carried out in aqueous solution. Due to their intense UV absorption, the compounds dissolve in water with a yellow colour. UV data, as summarized in Table 2, refer to solutions in distilled water.

Aqueous solutions of the respective compounds were irradiated in quartz cuvettes by the light of a xenon high-pressure lamp. Concentrations were chosen such that UV spectra could be recorded directly without any dilution ($c \approx 6.3 \times 10^{-5}$ mol l^{-1}, pH 2). The solutions were acidified with hydrochloric acid to pH 2 to avoid a reaction of the photochemically generated diazonium compounds with sulphite ions, re-forming the diazosulphonates ($\mathrm{Ar{-}N{=}N{-}SO_3^- \rightleftharpoons Ar{-}N_2^+ + SO_3^{2-}}$). This reaction is possible at pH 7, but impeded at pH 2. In the latter case, the concentration of sulphite is negligibly small due to the equilibrium $\mathrm{SO_3^{2-} + H^+ \rightleftharpoons HSO_3^-}$ (pK_s=7.2); the hydrogensulphite ion is not capable of coupling with the diazonium ion.

In the case of long-chain compounds (C10, C12), photolysis sometimes results in precipitation of the final product(s) from the solutions at longer irradiation times, which causes an increase in the background of the UV spectra by scattering. To avoid this problem, compounds with a shorter hydrophobic part (C6/E, C6/A) were examined in detail. Although these compounds are not surfactants (see Section 2.3) and in any case were irradiated in a monomolecular dissolved state due to the low photolysis concentration (approximately 6.3×10^{-5} mol l^{-1}), we assume that the photochemistry of the diazosulphonate group does not change dramatically with aggregation. For C6/E and C6/A, the change in UV absorption with irradiation time is shown in Figs. 3 and 4 respectively.

In the case of C6/E, a continuous decrease in UV absorption, together with a hypsochromic shift from 293.5 nm (λ_{max} of C6/E) to about 275 nm, can be observed. Contrary to this behaviour, during the photolysis of C6/A, an initial increase in absorption occurs within the first few seconds, combined with a small bathochromic shift from 331.5 nm (λ_{max} of C6/A) to about 336 nm. At longer irradiation times, the absorption decreases continuously as observed for C6/E. We have found in the case of the 4-*n*-alkylbenzenediazosulphonate surfactants [1] that photolysis proceeds via the corresponding diazonium salt of the diazosulphonate ($Ar-N=N-SO_3^- \rightarrow Ar-N_2^+ + SO_3^{2-} \rightarrow Ar-X + N_2 + SO_3^{2-}$). Therefore the respective diazonium salts of C6/E and C6/A were synthesized as described in Section 3 and then photolysed under the same conditions (Figs. 5 and 6).

The following arguments support the sequence of photolysis steps given above (photolysis via the diazonium compound).

(1) Both diazonium salts (4-(hexanoyloxy)benzenediazonium chloride, $C6/E/N_2^+$; 4-(hexanoylamino)benzenediazonium chloride, $C6/A/N_2^+$) exhibit absorption maxima at the wavelengths at which the maxima are observed to shift during diazosulphonate photolysis. Contrary to $C6/E/N_2^+$ ($\lambda_{max}=275$ nm), the maximum of $C6/A/N_2^+$ ($\lambda_{max}=336$ nm) exhibits a bathochromic

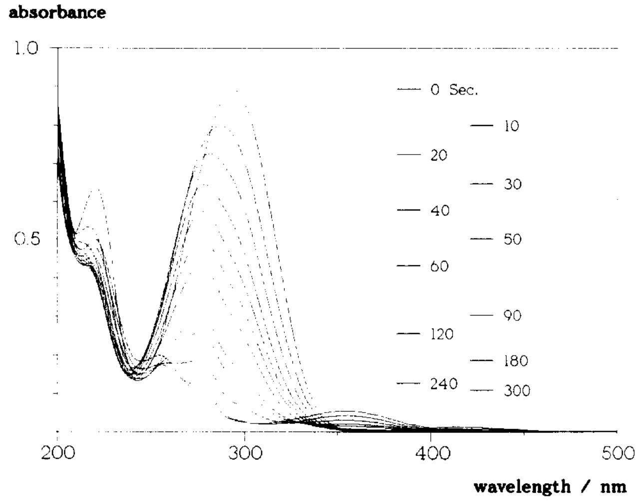

Fig. 3. Photolysis of diazosulphonate C6/E in water at room temperature; $c_0=6.2\times10^{-5}$ mol l^{-1}, pH 2.

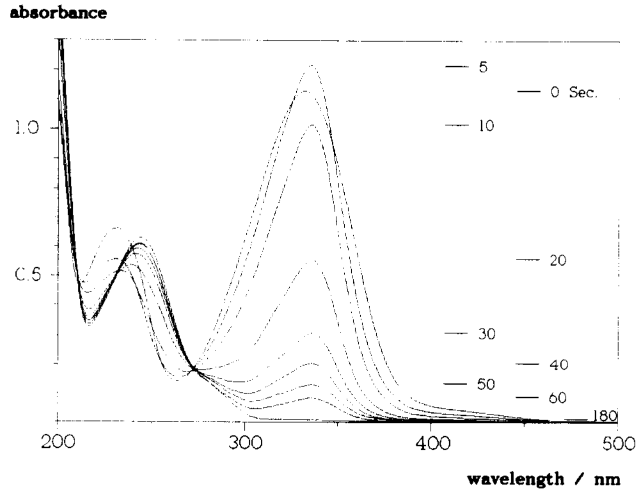

Fig. 4. Photolysis of diazosulphonate C6/A in water at room temperature; $c_0=6.3\times10^{-5}$ mol l^{-1}, pH 2.

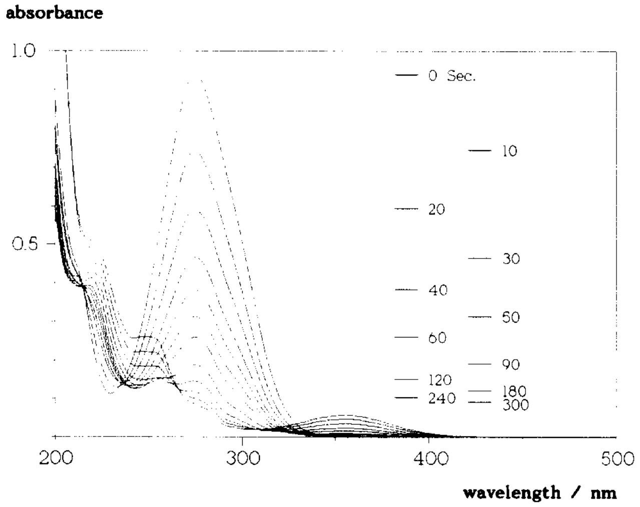

Fig. 5. Photolysis of the corresponding diazonium salt of C6/E in water at room temperature; $c_0=6.2\times10^{-5}$ mol l^{-1}, pH 2.

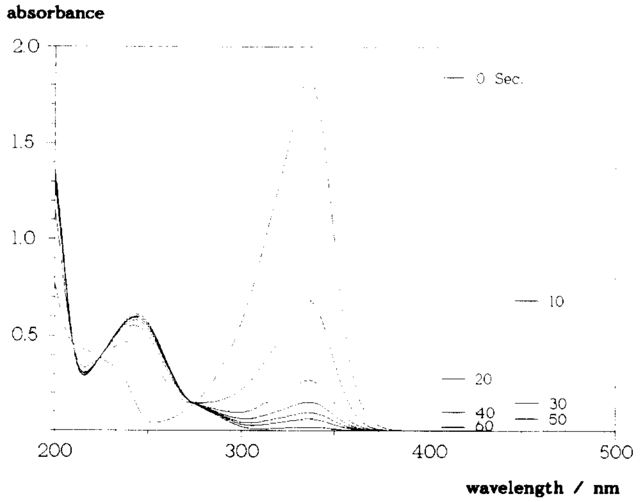

Fig. 6. Photolysis of the corresponding diazonium salt of C6/A in water at room temperature; $c_0=6.3\times10^{-5}$ mol l^{-1}, pH 2.

shift with respect to the absorption maximum of the corresponding diazosulphonate. This matches the course of the shift in the absorption maximum during diazosulphonate photolysis.

(2) The high absorption coefficient of C6/A/N_2^+ at 336 nm (λ_{max}) explains the initial increase in absorption during the photolysis of the diazosulphonate C6/A. The absorption coefficient was not determined exactly for C6/A/N_2^+, but a value of $\epsilon = 30\,200$ at λ_{max}, as given in the literature for C2/A/N_2^+ (4-acetylaminobenzenediazonium chloride) [2], is a good reference point (for comparison, $\epsilon = 18\,200$ for C6/A at 331.5 nm (λ_{max})).

(3) The UV spectra for total photolysis of both diazosulphonates are in good agreement with the spectra for total photolysis of the respective diazonium salts.

(4) Photolysis of both diazonium salts proceeds on a time scale which is compatible with the overall photolysis rate observed for the diazosulphonates.

On the basis of earlier results [1], we expected the corresponding phenolic compound as the main final product of diazosulphonate and diazonium photolysis. Fig. 7 shows the final spectrum of photolysis of both diazosulphonate C6/A and the diazonium compound C6/A/N_2^+ in comparison with the UV spectrum of 4'-acetamidophenol (obtained from Aldrich; a shorter alkyl chain of C2 should not influence the UV spectrum essentially compared with a C6 alkyl chain). A very good agreement clearly establishes the corresponding phenol as the main product of photolysis.

In the case of C6/E, a comparison of the kind described above could not be carried out as the corresponding phenolic compound was not available. However, in this case it is safe to assume that the corresponding phenol (4-hydroxyphenyl hexanoate) is the main photolysis product. A growing absorption near 355 nm at the end of diazosulphonate and diazonium photolysis indicates the presence of a further product.

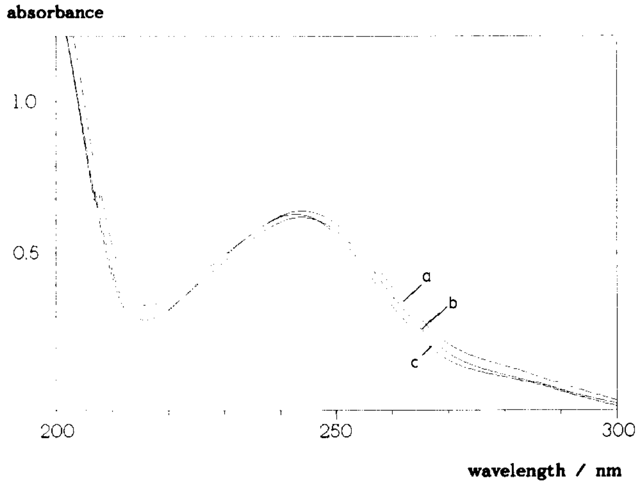

Fig. 7. UV spectra after complete photolysis of C6/A (from Fig. 4, curve a) and the corresponding diazonium compound (from Fig. 6, curve b), together with the UV spectrum of 4-acetamidophenol (curve c). All compounds were dissolved at the same concentration of 6.3×10^{-5} mol l^{-1}.

The higher rate observed for the photolysis of C6/A (total photolysis proceeds in about 180 s compared with about 300 s in the case of C6/E; see Figs. 3 and 4) can be explained by the stronger absorption of C6/A in the visible part of the UV spectrum, matching the stronger emission of the Xe lamp in this region [3]. The same applies to the respective diazonium compounds. The red shift in the UV absorption of diazosulphonate C6/A compared with C6/E can be explained by the stronger electron-donating interaction of the amide bond with the aromatic phenyldiazosulphonate moiety. In Ref. [4], a Hammett substituent constant of $\sigma_p = 0.00 \pm 0.1$ is given for the acetylamino group ($-NH-CO-CH_3$), in contrast with $\sigma_p = 0.31 \pm 0.1$ for the acetoxy group ($-O-CO-CH_3$).

2.5. *Thermolysis*

Thermolysis experiments were carried out in water (observed by UV spectroscopy) and in the solid phase (monitored by differential scanning calorimetry (DSC)). DSC data for the decomposition of the solid diazosulphonates in an air or nitrogen atmosphere are summarized in Table 3. In all cases decomposition proceeds above 150 °C. The diazosulphonate compounds can therefore be stored at room temperature in the dark without decomposition.

Thermolysis in water was examined for the diazosulphonate compounds C6/E and C6/A. Compared with C6/E, the diazosulphonate C6/A is thermally more stable, with a half-life of about 29 h, obtained from the decrease in the UV absorption maximum at a temperature of 94 °C. Decomposition was not examined in detail, as no further characteristic absorption maxima occurred during the course of thermolysis.

In contrast with C6/A, where thermolability is due to the decomposition of the diazosulphonate group, the diazosulphonate C6/E is extremely labile via hydrolysis of the ester bond, even at a value of pH 7. Two examples of thermolysis under basic (pH 9) and acidic (pH 6) conditions at a temperature of 50.5 °C are displayed in Figs. 8–10.

At pH 9, a fast decrease in diazosulphonate absorption at 293.5 nm can be observed, accompanied by the occurrence of two new absorption maxima at about 348.5 and 400 nm (Fig. 8), which are ascribed to *p*-quinonediazide and phenolate species. A detailed description of the possible reaction paths, which consist of different pH-dependent equilibria, is displayed in Fig. 11. Under basic conditions, the ester C6/E is rapidly hydrolysed to the corresponding phenolate anion; this is in equilibrium with the corresponding phenol under moderately basic conditions (for 4-hydroxybenzenediazosulphonate, a pK_s value of 7.5 was determined as

Table 3
DSC data for the decomposition of the solid diazosulphonates in an air or nitrogen atmosphere (T_{max}, maximum of the DSC curve (heating rate, 10 K min^{-1}); ΔH_{dec}, decomposition enthalpy)

Compound	$T_{max, N2}$ (°C)	$\Delta H_{dec, N2}$ (kJ mol^{-1})	$T_{max, air}$ (°C)	$\Delta H_{dec, air}$ (kJ mol^{-1})
C6/E	248.5	−99	201.0	−202
C8/E	250.0	−101	201.0	−203
C10/E	248.0	−90	187.5	−258
C12/E	246.0	−96	190.0	−244
C6/A	274.0	−90	271.5	−225
C8/A	275.0	−92	268.5	−201
C10/A	275.0	−88	255.5	−182

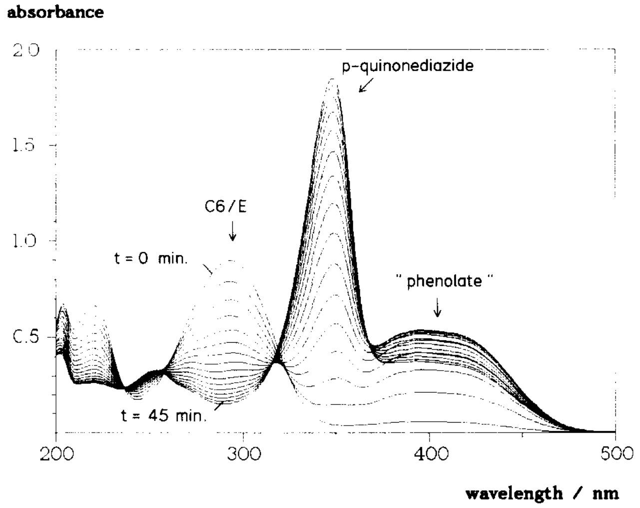

Fig. 8. Thermolysis of diazosulphonate C6/E in aqueous solution (pH 9) at a temperature of 50.5 °C during the first 45 min; $c_0 = 6.3 \times 10^{-5}$ mol l^{-1}; time interval between the recorded UV spectra, 3 min.

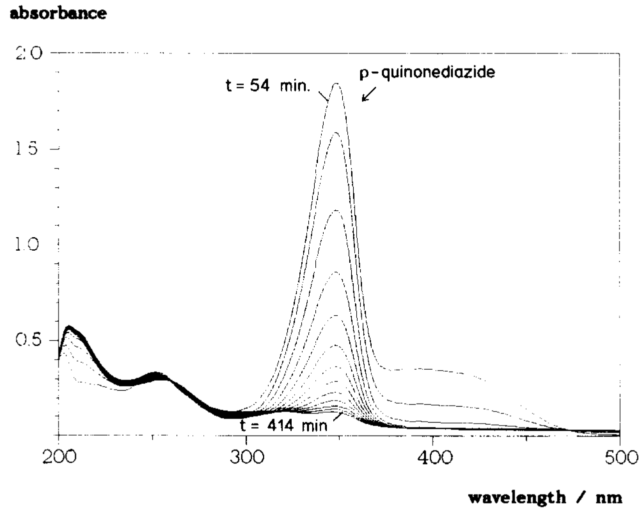

Fig. 9. Thermolysis of diazosulphonate C6/E in aqueous solution (pH 9) at a temperature of 50.5 °C (continuation of Fig. 8); time interval between the recorded UV spectra, 30 min.

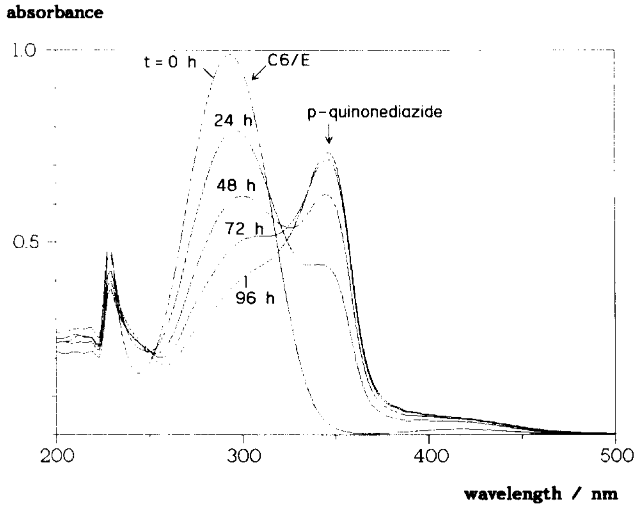

Fig. 10. Thermolysis of diazosulphonate C6/E in aqueous solution (pH 6) at a temperature of 50.5 °C; $c_0 = 6.9 \times 10^{-5}$ mol l^{-1}; time interval between the recorded UV spectra, 24 h.

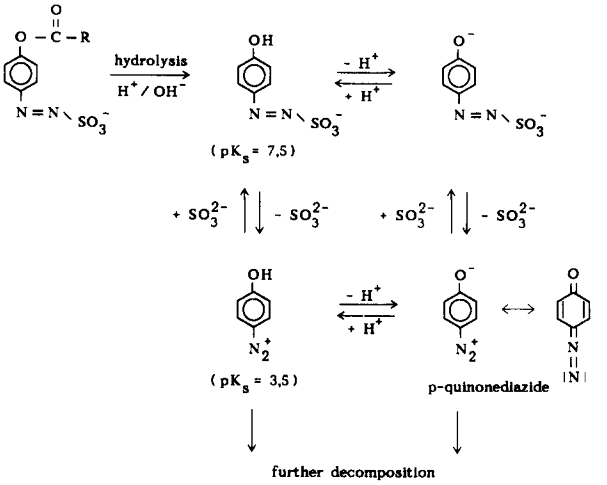

Fig. 11. Survey of different possible reaction paths for the thermolysis of C6/E in water at different pH values (the pH-dependent equilibrium $SO_3^{2-} + H^+ \rightleftharpoons HSO_3^-$ was not included for clarity).

described in Section 3). In a further equilibrium reaction the thermolabile phenolate reacts quickly to the corresponding *p*-quinonediazide by elimination of sulphite

(SO_3^{2-}). An absorption coefficient of $\epsilon = 45\,000$ at 350 nm (λ_{max}) is given in that literature for *p*-quinonediazide [5], which explains the strong increase in UV absorption in this region during the first 45 min of thermolysis. The thermal decomposition of *p*-quinonediazide during further photolysis is observed on a longer time scale, as shown in Fig. 9. The thermolysis of *p*-quinonediazide at pH 9 on a time scale of a few hours cannot be ascribed to the presence of hydroxide ions alone; in a separate experiment we found that thermolysis of pure *p*-quinonediazide requires several days under the same conditions (buffer solution of pH 9, $T = 50$ °C). Presumably the presence of phenolate hastens the thermal decomposition, as the addition of about an equal amount of 4-nitrophenol (p$K_s = 7.2$ [6]) to the buffered pure *p*-quinonediazide solution mentioned above (pH 9, $T = 50$ °C) has a strong accelerating effect. This decomposition mechanism was not examined further.

Under acidic conditions, thermolysis of C6/E is much slower and proceeds over a period of several days, as shown in Fig. 10 at pH 6 for the first 96 h. Again thermolysis is via *p*-quinonediazide, presumably due to deprotonation of the 4-hydroxybenzenediazonium salt (p$K_s = 3.5$ [6], product of sulphite elimination of 4-hydroxybenzenediazosulphonate), or via the "phenolate pathway", as a small amount of phenolate is present even at pH 6 (pK_s of 4-hydroxybenzenediazosulphonate, 7.5). Under acidic conditions, the less efficient hydrolysis, together with both the higher thermal stability of 4-hydroxybenzenediazosulphonate (compared with the corresponding phenolate) and the higher stability of *p*-quinonediazide, slows down the overall decomposition process.

3. Experimental section

3.1. Chemicals

Unless stated otherwise the chemicals used for synthesis were commercial products from Merck or Aldrich. The carboxylic acid chlorides from Merck were distilled before use and stored under argon.

3.2. General instructions for the synthesis of diazosulphonates

Due to the photolability of the diazosulphonates, light was avoided during all synthesis procedures (darkened room or covering of the flasks with aluminium foil is recommended).

3.3. Synthesis of sodium 4-(acyloxy)benzenediazosulphonates

3.3.1. Sodium 4-hydroxybenzenediazosulphonate

4-Aminophenol hydrochloride was diazotized by standard procedures ($NaNO_2$/HCl/H_2O) and coupled with sulphite to yield 4-hydroxybenzenediazosulphonate. The yellow compound was recrystallized from water. Proton nuclear magnetic resonance (^{1}H-NMR) (dimethylsulphoxide-d_6 (DMSO-d_6)): δ 6.80–7.05 (m, 2H), 7.55–7.80 (m, 2H), 10.10–10.45 (s, 1H; –OH). IR (KBr): ν (cm^{-1}) 3600–3000 (O–H), 1595, 1510, 1478 (ar C=C), 1044 (S=O).

3.3.2. Sodium 4-(acyloxy)benzenediazosulphonates

Sodium 4-hydroxybenzenediazosulphonate, suspended in absolute tetrahydrofuran, was acylated to the corresponding esters by the reaction with carboxylic acid chlorides of different chain lengths (C6/E, hexanoic acid chloride; C8/E, octanoic acid chloride; C10/E, decanoic acid chloride; C12/E, dodecanoic acid chloride; twofold excess of carboxylic acid chloride). Triethylamine was added to the reaction mixture to capture the HCl gas produced. After the reaction was completed, tetrahydrofuran and excess triethylamine were distilled off in vacuum. The residue was stirred several times with diethylether (for removal of excess acid chloride) and finally with a 17 wt.% aqueous solution of Na_2CO_3 (for removal of triethylamine hydrochloride). The yellow compounds were recrystallized twice from water.

Sodium 4-(hexanoyloxy)benzenediazosulphonate (C6/E). ^{1}H-NMR (DMSO-d_6): δ 0.70–0.98 (m, 3H), 1.10–1.48 (m, 4H), 1.48–1.75 (m, 2H), 2.50–2.70 (t, 2H), 7.20–7.40 (m, 2H), 7.70–7.90 (m, 2H). IR (KBr): ν (cm^{-1}) 2957, 2930, 2872, 2860 (C–H), 1751 (C=O), 1597, 1510 (C=C), 1260, 1234, 1071 (S=O). $C_{12}H_{15}N_2O_5SNa$ (322.30): calculated: C, 44.72; H, 4.69; N, 8.69; S, 9.95; found: C, 44.90; H, 4.68; N, 8.81; S, 9.93.

Sodium 4-(octanoyloxy)benzenediazosulphonate (C8/E). ^{1}H-NMR (DMSO-d_6): δ 0.70–0.98 (m, 3H), 1.10–1.48 (m, 8H), 1.48–1.75 (m, 2H), 2.50–2.70 (t, 2H), 7.20–7.40 (m, 2H), 7.70–7.90 (m, 2H). IR (KBr): ν (cm^{-1}) 2957, 2926, 2872, 2853 (C–H), 1751 (C=O), 1597, 1510 (C=C), 1260, 1234, 1071 (S=O). $C_{14}H_{19}N_2O_5SNa$ (350.35): calculated: C, 47.99; H, 5.47; N, 8.00; S, 9.15; found: C, 47.82; H, 5.93; N, 7.79; S, 9.43.

Sodium 4-(decanoyloxy)benzenediazosulphonate (C10/E). ^{1}H-NMR (DMSO-d_6): δ 0.70–0.98 (m, 3H), 1.10–1.48 (m, 12H), 1.48–1.75 (m, 2H), 2.50–2.70 (t, 2H), 7.20–7.40 (m, 2H), 7.70–7.90 (m, 2H). IR (KBr): ν (cm^{-1}) 2955, 2918, 2872, 2851 (C–H), 1751 (C=O), 1597, 1507 (C=C), 1260, 1234, 1071 (S=O). $C_{16}H_{23}N_2O_5SNa$ (378.40): calculated: C, 50.78; H, 6.13; N, 7.40; S, 8.47; found: C, 51.05; H, 6.16; N, 7.55; S, 8.41.

Sodium 4-(dodecanoyloxy)benzenediazosulphonate (C12/E). ^{1}H-NMR (DMSO-d_6): δ 0.70–0.98 (m, 3H), 1.10–1.48 (m, 16H), 1.48–1.75 (m, 2H), 2.50–2.70 (t, 2H), 7.20–7.40 (m, 2H), 7.70–7.90 (m, 2H). IR (KBr): ν (cm^{-1}) 2955, 2918, 2872, 2849 (C–H), 1751 (C=O), 1600, 1510 (C=C), 1260, 1236, 1071 (S=O). $C_{18}H_{27}N_2O_5SNa$ (406.45): calculated: C, 53.19; H, 6.70; N, 6.89; S, 7.89; found: C, 53.53; H, 6.72; N, 6.72; S, 7.95.

3.4. *Synthesis of sodium 4-(acylamino)benzenediazosulphonates*

3.4.1. *Sodium 4-aminobenzenediazosulphonate*

The synthesis was performed as described in Ref. [7].

3.4.2. *Sodium 4-(acylamino)benzenediazosulphonates*

Synthesis of the amides proceeded according to the preparation of the sodium 4-(acyloxy) benzenediazosulphonates, as described above, with sodium 4-aminobenzene diazosulphonate instead of sodium 4-hydroxybenzenediazosulphonate.

Sodium 4-(hexanoylamino)benzenediazosulphonate (C6/A). ^{1}H-NMR (DMSO-d_6): δ 0.75–0.95 (m, 3H), 1.15–1.45 (m, 4H), 1.45–1.70 (m, 2H), 2.25–2.42 (t, 2H), 7.62–7.88 (m, 4H), 10.10–10.28 (s, 1H, –CO–NH–). IR (KBr): ν (cm^{-1}) 3322 (N–H), 2955, 2930, 2872, 2860 (C–H), 1667 (C=O), 1601, 1512 (C=C), 1537 (C–N) δ (N–H), 1260, 1234, 1071 (S=O). $C_{12}H_{16}N_3O_4SNa$ (321.31): calculated: C, 44.85; H, 5.02; N, 13.08; S, 9.98; found: C, 44.71; H, 5.00; N, 12.90; S, 10.15.

Sodium 4-(octanoylamino)benzenediazosulphonate (C8/A). ^{1}H-NMR (DMSO-d_6): δ 0.75–0.95 (m, 3H), 1.15–1.45 (m, 8H), 1.45–1.70 (m, 2H), 2.25–2.42 (t, 2H), 7.62–7.88 (m, 4H), 10.10–10.28 (s, 1H, –CO–NH–). IR (KBr): ν (cm^{-1}) 3326 (N–H), 2955, 2922, 2872, 2851 (C–H), 1668 (C=O), 1601, 1512 (C=C), 1537 (C–N) δ(N–H), 1258, 1234, 1071 (S=O). $C_{14}H_{20}N_3O_4SNa$ (349.37): calculated: C, 48.13; H, 5.77; N, 12.03; S, 9.19; found: C, 47.90; H, 5.76; N, 11.88; S, 9.38.

Sodium 4-(decanoylamino)benzenediazosulphonate (C10/A). ^{1}H-NMR (DMSO-d_6): δ 0.75–0.95 (m, 3H), 1.15–1.45 (m, 12H), 1.45–1.70 (m, 2H), 2.25–2.42 (t, 2H), 7.62–7.88 (m, 4H), 10.10–10.28 (s, 1H, –CO–NH–). IR (KBr): ν (cm^{-1}) 3331 (N–H), 2955, 2918, 2872, 2850 (C–H), 1670 (C=O), 1601, 1512 (C=C), 1535 (C–N) δ(N–H), 1260, 1234, 1071 (S=O). $C_{16}H_{24}N_3O_4SNa$ (377.42): calculated: C, 50.91; H, 6.41; N, 11.13; S, 8.49; found: C, 51.12; H, 6.23; N, 11.13; S, 8.63.

3.5. *Synthesis of the diazonium salts*

The synthesis is described in Section 3.7.

3.6. *Krafft temperature measurements*

The procedure is described in Ref. [1].

3.7. *Photolysis experiments*

The photolysis conditions and procedures are given in Ref. [1]. The only difference involves slight variations of the photolysis configuration. In the experiments described here, the distances between the irradiated sample and the light source and shutter are 60 cm and 15 cm respectively.

The irradiated aqueous diazonium salt solutions were prepared as follows. The corresponding diazonium salt of the compound C6/E (4-(hexanoyloxy)benzenediazonium chloride) was prepared by acylation of 4-nitrophenol with hexanoic acid chloride, followed by catalytic reduction (PtO_2/H_2) of the nitro group of the ester obtained to the respective aromatic amine (4-aminophenyl hexanoate). The latter compound was diazotized by standard procedures ($NaNO_2/HCl/H_2O$) to the diazonium salt. Thereafter, one drop of the concentrated solution obtained in this way was diluted with acidified Millipore water (pH 2) to the appropriate photolysis concentration (6.3×10^{-5} mol l^{-1}). Synthesis of the corresponding diazonium salt of the compound C6/A (4-(hexanoylamino)benzenediazonium chloride) followed the same sequence of reaction steps as described above, with 4-nitroaniline as the starting compound instead of 4-nitrophenol.

3.8. *Thermolysis experiments*

Thermolysis of the solid diazosulphonates and C6/A in water ($c \approx 6 \times 10^{-5}$ mol l^{-1}) was carried out according to the procedures described in Ref. [1].

Thermolysis of aqueous solutions of C6/E at different pH values ($c \approx 6.5 \times 10^{-5}$ mol l^{-1}) was observed in a double-beam UV spectrometer (U-3000/Hitachi). Due to the extreme hydrolysis sensitivity of the compound under basic conditions even at room temperature, the pure buffer solution was placed in the cuvette and heated to the thermolysis temperature by means of a thermostatically controlled cuvette holder. To establish the desired reactant concentration, one drop of a concentrated solution of C6/E in water (at room temperature) was added by a calibrated pipette. After shaking, the UV spectra were recorded in intervals.

The buffer solutions used were commercial products from Merck, and were degassed for about 30 min in the vacuum of a water jet pump before use.

The pure *p*-quinonediazide solution, mentioned in Section 2.5, was prepared by diazotization of 4-hydroxyaniline by standard procedures, and by adding one drop of this concentrated solution to a large amount of buffer solution (pH 9). Under basic conditions, the 4-hydroxybenzenediazonium species ($pK_s = 3.5$) reacts to give *p*-quinonediazide by phenolic deprotonation.

The pK_s value of sodium 4-hydroxybenzenediazosulphonate (p$K_s = 7.5$) was determined as follows. Buffer solutions with equal concentrations of sodium 4-hydroxybenzenediazosulphonate ($c = 6.8 \times 10^{-5}$ mol l^{-1}, at room temperature) were prepared, spanning the range from pH 4 to pH 12. For each buffer solution, the relative amounts of phenol and phenolate were determined by UV spectroscopy. A plot of the percentage of phenolate or the percentage of phenol against the pH value yields the pK_s value as the point at which the concentrations of phenol and phenolate are equal.

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