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Photochemistry of Aromatic Sulphonyl Compounds

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The spectra of aromatic sulphonyl compounds $ArSO_2X$—sulphonic acids, their derivatives, and sulphones X = OH, OAlk, OAr, Hal, NH_2, N_3, Alk, Ar)—are examined, information is reported on the photoreactions, and modern views are given on the mechanism of these processes. A list of 143 references is included.

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I. INTRODUCTION

Aromatic sulphonic acids, their derivatives (esters, amides, halides, and azides), and sulphones are extremely numerous and important compounds in organic chemistry, of both purely theoretical and practical interest. In contrast to dark chemistry and the photochemistry of other sulphur-containing compounds, until fairly recently hardly any investigation had been made of the photochemical properties of the present group of compounds. The chemistry of their excited states has begun to be developed only during the past 10–15 years in connection with the appearance of new physicochemical methods and the improvement of photochemical experimental techniques. A considerable number of publications have appeared in this field, but they have not been summarised in the Soviet literature†, and an attempt is made in the present paper. The literature has been covered up to 1973 inclusive.

† A review of the photochemistry of aromatic sulphonic acids will be found in Ref. 1.

II. SPECTRA OF COMPOUNDS $ArSO_2X$

The sulphonyl group SO_2, present in all the compounds under review, contains positively charged sulphur without a lone pair of electrons and on the whole has a planar structure[2]. Most investigators consider that, as a consequence, conjugation of the π-electron system of the aromatic residue with the sulphonyl group and through the latter with the X moiety is absent. In sulphonic acids and esters, sulphonamides, and sulphonyl halides, therefore, the effect of the SO_2X substituent is regarded as purely inductive or one in which the inductive effect predominates considerably over the conjugation effect[3,4]. The electronic absorption spectrum of the aromatic ring system is little affected in these compounds, being determined by the chromophores of the unsubstituted compound weakly perturbed by the sulphonyl group. Furthermore, even this slight effect of the SO_2X group is smaller the larger the number of aromatic rings in the fused structure. Introduction of an SO_2X substituent has little effect also on the

energy characteristics of photoexcited states of the aromatic system.

Nevertheless, attempts were sometimes made to reveal conjugation of the aromatic ring with the SO_2X substituent, e.g. in compounds $C_6H_5SO_2X$ (X = OH, OCH_3, Hal), from a study of the ultraviolet spectra [5,6]. The results reported below, however, largely contradict the authors' arguments.

The main spectral features of aromatic sulphonic acids attributable to the sulphonyl group are apparent also in such derivatives as esters, amides, and halides, which is confirmed not only by their electronic spectra [3]. Thus the same conclusion is reached from an investigation of these compounds by Raman and infrared spectroscopy (in particular the effect of nuclear substituents on the spectra) [7]. This permits us to use the sulphonic acids of benzene, naphthalene, anthracene, and anthraquinone, which are most often subjected to photochemical reactions, to examine the above features of the effect of the SO_2X group on the spectral characteristics of aromatic compounds.

Three absorption bands—at 210 nm (ϵ = 5000), 255–272 nm (ϵ = 200–400, split into four narrow peaks), and 293 nm (weak)—are present in the ultraviolet spectrum of aqueous benzensulphonic acid (I) [8,9]. The appearance of a band in the region of 270 nm is attributed [9] to the electron-accepting properties of the sulpho-group, evident in a displacement of electron density from the benzene ring to the positively charged sulphur atom.

Among the anilinesulphonic acids (IIa–c) sulphanilic acid (IIc) has been most thoroughly studied. Spectral investigations, as well as conductivity measurements on its aqueous solutions [10], have shown that it is not an internal salt [11] or a zwitterion [12]. In contrast to metanilic (IIb) and orthanilic (IIa) acids, which have absorption maxima at 293 and 294 nm respectively with $\lg\epsilon$ = 3.21 and 3.43, the spectrum of (IIc) has a shoulder (278–302 nm) in this region, and at shorter wavelengths a band develops from the second absorption band of benzenesulphonic acid, which is sometimes explained by partial conjugation of amino- and sulpho-groups through the benzene ring [10]. On protonation of the amino-group in an acid medium the spectra of all of the anilinesulphonic acids (IIa–c) approach the spectrum of benzenesulphonic acid [10,13], but in alkaline solutions that of aniline (III) [14].

Neither benzenesulphonic acid (I) nor its salts luminesce, owing to deactivation of the benzene ring and localisation of the π-electrons under the influence of the sulpho-group [15]. Delocalisation of π-electrons, due to the strong effect of the amino-group, is dominant with the anilinesulphonic acids (IIa–c). Sodium sulphanilinate luminesce in water at 293°K (Φ = 0.07) [16]. The phosphorescence spectrum of crystals of this acid contain [17] two bands at 405–460 and 460–540 nm, which decay at different rates and are assigned [17,18] to two triplet levels (51.2 and 69.2 kcal $mole^{-1}$).

The spectra of naphthalene-1- and -2-sulphonic acids (IVa) and (IVb), as well as that of naphthalene itself (V), contain three electronic bands—^1L_b, ^1L_a, and ^1B_b at 290–320, 250–290, and 210–240 nm respectively—corresponding to $\pi\pi^*$-transitions [19–21] (Platt's classification [22]). The considerable difference between the molecular orbitals of the 1- and 2-isomers (IVa) and (IVb) is responsible for the difference (though slight) between their absorption spectra [23]. The presence of a 1-sulpho-group leads to a bathochromic shift of the ^1L_a and ^1B_b bands, but the 2-isomer shows a bathochromic shift of the ^1L_b band; intensification of the longer-wavelength band is observed with both isomers. No change in direction of the moments of the electron transitions was observed on migration of the substituent from the 1- to the 2-position in the above isomers (IVa) and (IVb) [24]. The direction of the transition moments is obviously unaffected not only by change in the position of the sulpho-group in the naphthalene ring system but also by its introduction into the ring. Substituents which undergo conjugation behave differently; they usually change the direction of the moments of certain transitions of fused aromatic systems [19,24]. As with naphthalene [25,26], the ^1L_b and ^1B_b transitions of its 1- and 2-sulphonic acids (IVa) and (IVb) are evidently parallel to the long symmetry axis x, while the ^1L_a transition is perpendicular to it.

Introduction of a 4-amino-group into naphthalene-1-sulphonic acid displaces the ^1B_b band to longer wavelengths and halves its intensity; the ^1L_a band undergoes a bathochromic shift, and its intensity is doubled [20,27]. This effect, as with the anilinesulphonic acids, is due to interaction of the amino-group with the naphthalene ring, which overlaps the effect of the sulpho-group. The absorption curve of naphthionic acid (VI) coincides in neutral and alkaline solutions with the spectrum of 1-naphthylamine (VII), but in acid solutions approximates to the spectrum of naphthalene-1-sulphonic acid (IVa) [20,27].

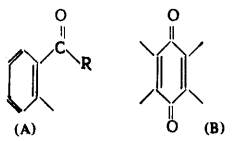
Both isomeric naphthalenesulphonic acids (IVa) and (IVb) fluoresce [28] in methanol–water matrices at 77°K. Naphthionic acid (VI) fluoresces intensely in aqueous solution (λ_{max} = 425 nm); the intensity increases over the pH range 0–6, and then remains constant with further increase in pH [29], owing to deprotonation of the amino-group. The quantum yield of the fluorescence of sodium 4-aminonaphthalene-1-sulphonate (VI) in water at 20°C is ~0.80. [30]

According to Smaller et al. [28] the fluorescence levels of naphthalene and of its 1- and 2-sulphonic acids differ by −1.2 and −1,3 kcal $mole^{-1}$ respectively, the corresponding differences for the phosphorescence levels being −0.35 and −0.09 kcal $mole^{-1}$. Thus E_{S^1} and E_{T^1} for the naphthalenesulphonic acids (IVa) and (IVb) are ~89 and ~60 kcal $mole^{-1}$. [28] If the effect of the sulpho-group in the aminosulphonic acid (VI) is also neglected, the energies of the excited states can be assumed to be close to those for 1-naphthylamine (VII) (E_{T^1} ~ 54 kcal $mole^{-1}$). [31]

Both groups of absorption bands of anthracene(VIII)—shorter-wavelength ^1B_b at 230–260 nm and longer-wavelength ^1L_a at 290–390 nm—exhibit a slight bathochromic shift on introduction of a sulpho-group. With anthracene-1-sulphonic acid (IXa) the shift of the ^1L_a band is ~5–6 nm, several times larger than that of the ^1B_b band. With anthracene-2-sulphonic acid (IXb), on the other hand, the relative shift of ^1B_b exceeds that of ^1L_a. [32] These results are consistent with indications [33,34] that the introduction of an electron-accepting substituent at position 1 or 9 in anthracene displaces the longer-wavelength band more strongly than the shorter-wavelength band. Popov's study [24] of the polarisation spectra of the anthracenesulphonic acids (IXa) and (IXb) suggests that, as with anthracene (VIII) [35], the moment of the transition $^1L_a \leftarrow {}^1A_1$ is parallel to the long x-axis of the molecule, while the moment of the transition $^1B_b \leftarrow {}^1A_1$ is parallel to the short y-axis. These sulphonic acids luminesce in solution, in contrast to other anthracene derivatives containing electron-accepting substituents (nitro, carboxy) that conjugate with the anthracene ring system [36–38]. On the assumption that the energy levels of excited states of these sulphonic acids differ little from the levels of anthracene, we can estimate them as E_{S^1} = 76 and 72.5 kcal $mole^{-1}$ for anthracene in solution and in the crystalline state, and E_{T^1} = 42.5 kcal $mole^{-1}$. [39]

Introduction of a sulpho-group at position 1 or 2 in

anthraquinone (X) produces a slight bathochromic shift (>5 nm) of the absorption bands with a slight increase in their intensity. The spectrum of anthraquinone itself (X) comprises six bands—at 243.5, 252.5, 262.8, 272, 325.5, and 405 nm—and is often regarded as resulting from the superposition of the spectra of two chromophores (A) and (B)[40]



(A) (B)

All these bands other than the last have been assigned to $\pi\pi^*$-electron transitions[41-44]. The moments of the transitions of bands at 252.5, 262,8, and 325.5 nm are polarised along the short y-axis of the molecule[42,44,45], and that of the 272-nm band is polarised along the long x-axis[45]. The chromophore of anthraquinone is sometimes regarded[46] as two weakly interacting *ortho*-disubstituted benzenes, the three $\pi\pi^*$-states of anthraquinone being associated with the ^1L_b, ^1L_a, and ^1B_b bands of benzene[22]. Hence the bands at 252.5, 325.5, and 272 nm are assigned to $^1B_b \leftarrow {}^1A_1$, $^1L_b \leftarrow {}^1A_1$, and $^1L_a \leftarrow {}^1A_1$ transitions in the benzene ring[44,47]. The absorption at 405 nm, which is so weak that it is not always evident, has given rise to the most contradictory conclusions[40,48]; its transition moment lies in the plane of the molecule, and is polarised along the x-axis[44]. The lifetime of the phosphorescent state on excitation in this band[49,50] and the shifts it undergoes in various solvents[51] have enabled it to be assigned quite confidently to an $n\pi^*$-level of anthraquinone. The assignment of the 405-nm absorption to a $\pi\pi^*$-transition, which was based on theoretical calculations[52], seems very questionable.

The bands in the electronic spectra of anthraquinone-1- and -2-sulphonic acids are assigned in the same way as with anthraquinone[53]. Differences between the isomers resulting from the position of the sulpho-group are more clearly evident in the infrared spectra[2]. The spectrum of the ion of the sulphonic acid (XII) in the solid state contains an absorption band corresponding to carbonyl-stretching vibrations at 1678 cm^{-1}; in the ionised form of the 1-isomer (XIa) this is split into two, at 1678 and 1692 cm^{-1}. The latter corresponds to the 9-carbonyl group, and results from donor–acceptor interaction of the SO_2O^- group with the quinoid system of the molecule. Band splitting is observed also with the covalent anthraquinone-1-sulphonic acid: the carbonyl frequency has fallen to 1684 and 1664 cm^{-1} (carbonyls at positions 10 and 9), and absorption appears at 3200 cm^{-1}, due to hydroxyl involved in an intramolecular hydrogen bond.

Photoexcitation of anthraquinone (X) and its sulphonic acids may transfer their molecules to $S_{\pi\pi^*}$, $S_{n\pi^*}$, $T_{\pi\pi^*}$, and $T_{n\pi^*}$ states. According to most authors[44,50,54,55] the lowest excited state is $T_{n\pi^*}$, above this is located the $S_{n\pi^*}$ level ($\Delta\nu \simeq 1000$ cm^{-1}), after which follow the $T_{\pi\pi^*}$ and $S_{\pi\pi^*}$ levels. This is counterbalanced by Nurmukhametov's view[50] that the $T_{\pi\pi^*}$ level is located between the $S_{n\pi^*}$ and $T_{n\pi^*}$ levels. Evidence is provided by the absence of fluorescence from the S_{n^*} level in solutions of anthraquinone and its derivatives, owing to the high efficiency of the $S_{n\pi^*} \rightarrow T_{\pi\pi^*}$ interconversion due to the increase of spin–orbital coupling between states of different electron configurations[56].

Luminescence has not been observed in solutions of anthraquinonesulphonic acids; formation is available only on the phosphorescence of (XII) in a matrix at low temperatures[57]. The presence of a sulpho-group in the anthraquinone molecule, whether at position 1 or 2, has hardly any effect on the arrangement of energy levels. The energy of the lowest triplet level of anthraquinone $T_{n\pi^*}$ is ~62.5 kcal $mole^{-1}$,[57,58] and ~62 kcal $mole^{-1}$ in the 2-sulphonic acid (determined from the phosphorescence spectrum)[57]. Because of the impossibility of determining experimentally the energy of the lowest singlet state $E_{S_{n\pi^*}}$ of anthraquinone and its sulphonated derivatives, values were calculated from the electronic absorption spectra[59]: the results were respectively 66.5, 64.3, and 64.6 kcal $mole^{-1}$ for anthraquinone and its 1- and 2-sulphonic acids.

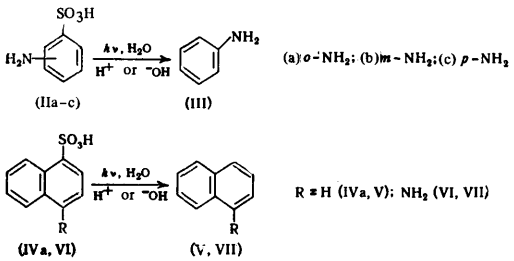
A rather different situation is found when the substituent X attached to the arylsulphonyl group possesses a sufficiently mobile π-electron system, as e.g. in diaryl sulphones and arenesulphonyl azides. Although published data on them are few and somewhat contradictory, the sulphonyl group in these compounds may be supposed to be better able to transmit the effect of conjugation. This is indicated in particular by a bathochromic shift (absorption in the range 230–245 nm) and a more than double hyperchromic effect on passing from methyl phenyl to diphenyl sulphone[60]. The measured dipole moments of a series of diaryl sulphones indicate a considerable displacement of electron density from the benzene rings to the sulphonyl group[61]. Since the sulphonyl sulphur atom does not possess a lone pair of electrons, which might have been involved in conjugation, it has been suggested[62] that 3*d*-orbitals of sulphur take part in this process.

There are indications that a similar effect occurs in aromatic sulphonyl azides[63]. The electronic spectra of the benzenesulphonyl azides that have been studied contain no bands in the region of 285 nm, where absorption by the benzene ring is absent, that might have been attributable to the azide group. The two bands observed—with a sharp maximum in the range 220–256 nm ($\lg\epsilon = 3.9$–4.5) and with a characteristic vibrational structure in the range 257–295 nm (2.5–3.4)—correspond to electron transitions between energy levels of the whole molecule. The red shifts of absorption bands I and II of benzene (by 19 and 10 nm respectively) on introduction of an azidosulphonyl group into the ring are substantially smaller than on introduction of an azido-group ($\Delta\lambda = 30$–45 nm). This is attributed[63] to a change in the character of the interaction between the substituent and the benzene ring: whereas the azido-group acts as an electron donor, the azidosulphonyl group possesses electron-accepting properties. The higher frequency of the azide-stretching vibrations in the infrared spectra of aromatic sulphonyl azides than in those of analogous aromatic azides indicates intensified localisation of bonds in the azide fragment under the influence of the sulphonyl group. Nevertheless, the correlations found between the absorption frequency of the azido-group (in the range 2120–2135 cm^{-1}) and the integral intensity of this band with the Hammett σ constants of substituents in the aromatic ring indicate that these substituents may be conjugated through the sulphonyl group with the π-electron system of the azido-group.

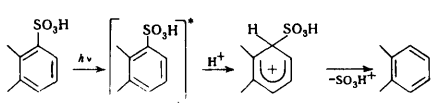
III. PHOTOCHEMICAL PROCESSES INVOLVING THE SULPHUR-CONTAINING GROUP

The simplest photochemical process directly involving the SO_2X group—elimination of the sulpho-group from certain aromatic sulphonic acids—can be accomplished by exposing their weakly acid, neutral, and weakly alkaline

aqueous solutions (pH 1–13) to ultraviolet radiation. The reaction takes place at room temperature, i.e. under conditions under which desulphonation does not take place in the dark. The yields of desulphonation products (III), (V), (VII), 1-sulphonic acids of naphthalene (IVa) and of 4-naphthylamine (VI), and *o*-, *m*-, and *p*-anilinesulphonic acids (IIa–b) increase in this sequence (from 2% to 50%) [64,65].



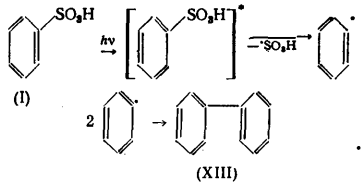
Both acidic and basic properties of aromatic molecules are strengthened by photoexcitation [66]. Which are realised in amphoteric excited states will depend on many factors. The electron affinity of the aromatic system increases in certain electrophilic photosubstitutions, e.g. isotopic hydrogen exchange, acylation, etc. [66,67]. By analogy with these reactions it has been postulated [65] that in acid media photodesulphonation involves hydrolytic detachment of the sulpho-group as a consequence of the enhanced basic properties of the aromatic ring. From the general consideration that, in comparison with the ground state, the basicity of triplet states varies less than that of singlet states, it seems more probable that a singlet excited state of the sulphonic acid takes part in the process [68]. Since the change in the acid–base properties of the π-electron system is very considerable (ΔpK_a may reach 25–30 [66]), it is quite likely that this increase in basic properties covers the decrease in hydrogen-ion concentration on passing from acid to neutral and weakly alkaline media in the pH range investigated [64] and, to all appearances, a mechanism of hydrolytic desulphonation



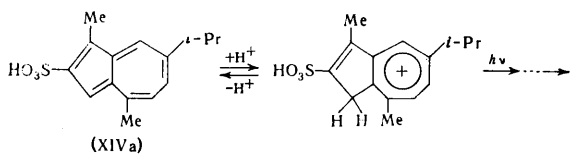
may operate not only in acid but also in neutral and even weakly alkaline media.

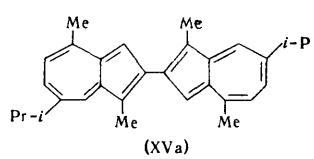
In alkaline aqueous solutions, on the other hand, reductive photodesulphonation with the hydroxide ion as electron donor is also possible [64]. It is interesting that the *meta*-isomer (IIb) is most readily desulphonated when alkaline solutions of the *o*-, *m*-, and *p*-sulphonic acids of aniline (IIa–c) undergo photolysis [64], as well as in the electrolytic detachment of the sulpho-group [69]. The reductive properties of the hydroxide ion in photochemical reactions with aromatic compounds have been discussed [70,71].

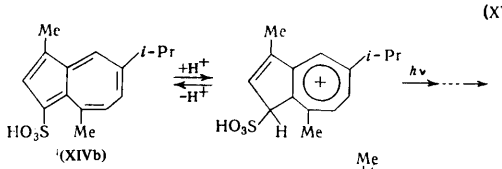
Elimination of the sulpho-group from benzenesulphonic acid (I) has a different mechanism [72]. Photolysis of its aqueous solutions produces biphenyl (XIII); the yield of the latter (up to 6%) is independent of pH (over the range 1–13 investigated) under identical conditions of irradiation, and the quantum efficiency of the process is below 10^{-4}. Desulphonation probably involves homolytic cleavage of the Ar–S bond in the photoexcited molecule of (I):

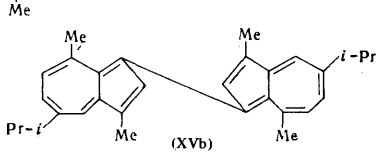


A similar result— the coupling of residues from the starting materials—is produced by photolysis of the protonated forms of guaiazulene-2- and -3-sulphonic acids (XIVa) and (XIVb). In 96% sulphuric acid they give respectively 2,2′- and 3,3′-biguaiazulyls (XVa) and (XVb) in up to 40% yield [73]:

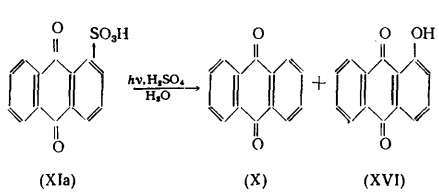








Only traces of anthraquinone (X) are formed by the irradiation of weakly acid (pH 1–7) aqueous anthraquinone-1-sulphonic acid (XIa). The efficiency of desulphonation is increased (up to 20%) by photolysis in 11 *N* sulphuric acid, and a small quantity (~3%) of 1-hydroxyanthraquinone (XVI) is obtained:



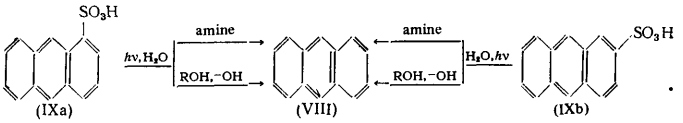
The sulpho-group of other anthraquinonesulphonic acids investigated—the 2-, 1,5-, and 1,8-acids (XII), (XIb), and (XIc)—remains unchanged under these conditions [74].

Considerable yields of anthraquinone (15–90%) have been obtained [64,65,75] by the irradiation of aqueous solutions of a sulphonate of (XIa) containing hydrazine, an aliphatic amine, or an alcohol with added alkali (the efficiency of photodesulphonation is lower with branched-chain alcohols [65]). Under identical conditions of photolysis the efficiences of complete desulphonation of anthraquinone-1,5- and -1,8-disulphonic acids (XIb) and (XIc) were substantially lower, not exceeding 10%; anthraquinone-2-sulphonic acid (XII) is not desulphonated.

Preliminary results indicate [65] that the rate of photodesulphonation is variable in the region of absorption by sulphonated anthraquinones: the maximum rate is obtained by photolysis in the far ultraviolet and decreases significantly with increase in wavelength of the exciting light.

Although elimination of the sulpho-group is effected in an alkaline medium, the initial compounds do not undergo hydroxylation (see beginning of this Section) [64], since alkoxide ions act as the main electron donor; furthermore, hydroxyl radicals, formed in considerably smaller quantity (than alkoxyl radicals), are removed by reaction with the alcohol.

Only traces of anthracene (VIII) are formed by the prolonged photolysis of aqueous solutions (in the presence of an amine) or alkaline aqueous–alcoholic solutions of anthracene-1- and -2-sulphonic acids (IXa) and (IXb) [75]:



Thus both the structure of the aromatic system and the position of the sulpho-group play important roles in this process.

When an anthraquinone-1-sulphonic acid undergoes photodesulphonation in alkaline aqueous–alcoholic and aqueous amine media, no component other than the acid is excited, and the formation of atomic hydrogen or a solvated electron as reductant is improbable. It has therefore been postulated [76] that electron transfer to the acid molecule, resulting from the enhancement of the electron-accepting properties of the latter on excitation, takes place in an excited complex of the sulphonic acid and the alkoxide ion or the amine [77]. Subsequent breakdown of the excited complex was assumed to yield the sulphite ion and an anthraquinone radical; detachment by the latter of a hydrogen atom from the alcohol or the amine yields anthraquinone.

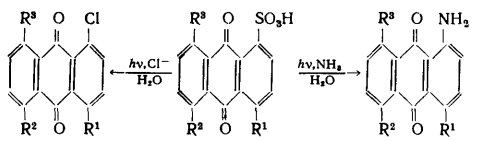
The photolysis of sulphonated anthraquinones (AS) in the above reducing media results in the corresponding products of their one- and two-electron reduction (the latter arise in secondary dark processes)—radical-ions ($AS^{\cdot -}$) and mono- and di-anions of anthraquinolsulphonic acids (ASH^-, AS^{2-})—which might have been intermediates in photodesulphonation, since in certain cases compounds of similar structure are able to eliminate electron-accepting substituents without excitation[78,79]. However, investigation of the effect of oxygen on photodesulphonation, together with the kinetics of the accumulation and destruction of the radical-anions and the formation of anthraquinone (A), has shown that the photodesulphonation of 1-sulphonated anthraquinones is actually a two-stage process with absorption of a light quantum at each stage. Absorption of the first quantum causes photoreduction of the substrate to the corresponding radical-anions with the appearance of products of their secondary dark reactions; absorption of the second quantum by one or all of the reduced forms yields anthraquinone as a result of the photochemical process and subsequent chemical reactions [80]:

$$AS \xrightarrow{h\nu} AS^*$$

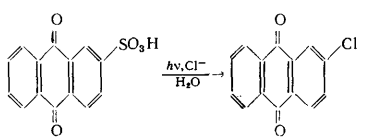
$$AS^* \xrightarrow{H_2O,ROH,\ NaOH} AS^{\cdot -} \longrightarrow ASH^- \ (AS^{=})$$

$$[AS^{\cdot -} \text{ and/or } ASH^-, AS^{=}] \xrightarrow{h\nu} [AS^{\cdot -} \text{ and/or } ASH^-, AS^{=}]^* \xrightarrow[[O_2]]{H_2O,RCH_2OH,\ NaOH} A$$

Irradiation of anthraquinone-1-sulphonic acids (XIa–g, l, m) in aqueous solutions containing chloride ions or ammonia entails replacement of the sulpho-group by a chlorine atom [81] or an amino-group [64]. Chlorination goes in quantitative yield, but the yields from photoamination do not exceed 20%, and the rate of formation of the corresponding amino-derivative decreases as the duration of exposure is increased. Such slowing down is due to secondary nuclear hydroxylation and amination of the initial anthraquinonesulphonate (see Section IV for these reactions), as the resulting water-soluble hydroxy- and amino-anthraquinonesulphonic acids inhibit substitution of the sulpho-group by filtering out the photochemically active light [82]. Special experiments on the effect of additions of such water-soluble acids on photoamination have shown that the assumed energy transfer from excited substrate molecules to by-product molecules [65] plays no appreciable part. Replacement of the sulpho-group in anthraquinone-2-sulphonic acid (XII) by a chlorine atom has a low yield (2%), but the sulpho-group in anthracenesulphonic acids (IXa) and (IXb) is replaced neither by chlorine nor by an amino-group.



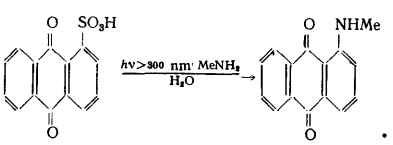
(XVIIa–g, l, m) (XIa–g, l, m) (XVIIIa–g, l, m)



(XII) (XIX)

a: $R^1=R^2=R^3=H$; (b) $R^1=R^3=H$, $R^2=SO_3H$; (c) $R^1=R^2=H$, $R^3=SO_3H$; (d) $R^1=SO_3H$, $R^2=R^3=H$; (e) $R^1=Cl$, $R^2=R^3=H$; (f) $R^1=R^3=H$, $R^2=Cl$; (g) $R^1=R^2=H$, $R^3=Cl$; (h) $R^1=NH_2$, $R^2=R^3=H$; (j) $R^1=R^3=H$, $R^2=NH_2$; (k) $R^1=R^2=H$, $R^3=NH_2$; (l) $R^1=R^3=H$, $R^2=NO_2$; (m) $R^1=R^2=H$, $R^3=NO_2$.

A 1-sulpho-group in anthraquinone does not undergo substitution by an alkylamino- or an arylamino-group: photodesulphonation occurs in the presence of aliphatic amines, as already mentioned, and no photoreaction takes place in the presence of aromatic amines. Methylamine is the only aliphatic amine in whose aqueous solutions both photodesulphonation and photosubstitution of the 1-sulphogroup in (XIa) takes place [65], the former process predominating on exposure to the complete spectrum from a mercury lamp. The second process predominates on exposure to light of wavelength exceeding 300 nm (the yield of 1-methylaminoanthraquinone (XX) is ~1%):



(XIa) (XX)

Photosubstitution of the 1-sulpho-group in (XIa) by a chlorine atom or an amino-group is not prevented by the presence of electron-accepting substituents (sulpho, chloro, nitro) at positions 4, 5, and 8 in the anthraquinone ring system, but the nature of the substituent and its position determine the rate of the process. Photosubstitution does

not take place when an electron-donating group (e.g. amino) is present at any of these three positions [74].

Light throughout the range of absorption is photochemically active in photosubstitution of the sulpho-group in anthraquinonesulphonates [82]. Photoamination and photochlorination of (XIa) have similar quantum efficiencies, which are independent of the wavelength of the exciting light over the range 250–435 nm. They vary between 10^{-4} and 10^{-3} depending on the reactant concentration: the quantum efficiency increases with the ammonia or chloride-ion concentration up to around molar, and then falls with further increase in concentration, probably owing to the concentration quenching of reactive excited states. In both cases photosubstitution is a one-photon process, as is confirmed by the linear dependence of its rate on the intensity of the light flux. The activation energy of photosubstitution (2.2–2.3 kcal mole^{-1} [83]) is typical of diffusion-controlled reactions [84]. Both photosubstitutions obey the simple Stern–Volmer equation on the addition of quenching agents (sodium iodide), with superposition of the straight lines corresponding to the observed relations when conducted simultaneously as competing reactions. Together with the equality of activation energy and closely similar quantum efficiencies of photoamination and photochlorination, this suggests that the processes have the same mechanism and involve a single excited state, probably $n\pi^*$.[65,82]

On the postulate that only the $n\pi^*$ level of the substrate is reactive, the inactivity of anthraquinonesulphonic acids with strong electron-donating substituents in reactions involving the sulpho-group can be explained by inversion of the energy levels on introduction of a donor substituent into the anthraquinonesulphonate ring system, as a consequence of which the unreactive $\pi\pi^*$ state becomes the lowest excited state of the molecule.

Two hypotheses have been put forward on the nature of the interaction between an excited substrate molecule and the reactant. According to the first the photochemical step in photochlorination is formation of a chlorine radical by electron transfer from a chloride ion to an excited molecule of anthraquinonesulphonic acid [65] (the possibility of such a process has been proved—Section IV); subsequent replacement of the sulpho-group by chlorine occurs as a dark radical process [85] with formation of the corresponding chloroanthraquinone (ACl):

$$AS \xrightarrow{h\nu} AS^* ,$$

$$AS^* + Cl^- \rightarrow AS^{\cdot-} + Cl^{\cdot} ,$$

$$Cl^{\cdot} + AS \rightarrow ACl .$$

Another possible radical substitution path does not involve formation of a chlorine radical as a kinetically independent species. On formation of the complex of the chloride ion and an excited molecule of anthraquinonesulphonic acid, almost simultaneously with the act of electron transfer, the resulting chlorine radical is trapped in a solvent cage by a sulphonate molecule in the ground (or an excited) state:

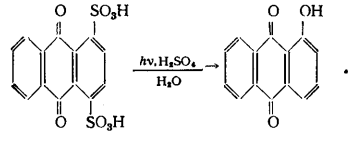
$$AS + \overset{\overset{AS}{+}}{Cl}\overset{\overset{+}{AS}}{} \xrightarrow{h\nu} ([AS \ldots Cl^-]^*, AS, AS^*) \longrightarrow ACl .$$

The second possible mechanism of photochlorination is nucleophilic substitution (in the classical sense of intermediate formation of a σ-complex) of the sulpho-group by a chloride ion in a photoexcited molecule of anthraquinonesulphonic acid [65]:

$$Cl^- + AS^* \rightarrow ACl .$$

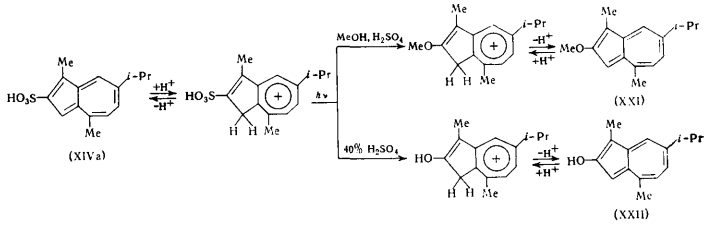
Analogous mechanisms may be suggested for the formation of aminoanthraquinones from anthraquinonesulphonic acids.

A sulpho-group in the anthraquinone ring system can sometimes be replaced photochemically by hydroxyl, as already noted. Whereas anthraquinone-1-sulphonic acid (XIa) yields only traces of 1-hydroxyanthraquinone (XVI), the latter is the main product (in 60% yield) of the photolysis of anthraquinone-1,4-disulphonic acid (XId) in 11 *N* sulphuric acid [74]:



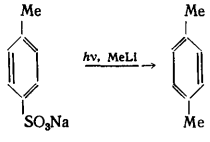
(XId) (XVI)

Considerably less study has been made of photosubstitution of the sulpho-group in systems other than anthraquinone. However, data have been published indicating that this group can be replaced also by hydroxyl, methoxyl, methyl, and the nitro-group. The first of these reactions occurs when guaiazulene-2-sulphonic acid (XIVa) is illuminated in 40% sulphuric acid, and the second on its photolysis in a mixture of methanol and sulphuric acid (3 : 2), with 40–50% yields [73]:



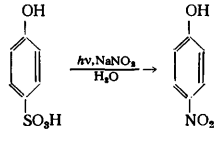
(XIVa) (XXI) (XXII)

The action of light on sodium toluene-*p*-sulphonate (XXIII) in the presence of methyl-lithium gives a yield of *p*-xylene (XXIV) reaching 4.5% as a result of nucleophilic substitution:



(XXIII) (XXIV)

hardly any reaction occurs in the dark (yield <1%) [86]. Photosubstitution of the sulpho-group in phenol-*p*-sulphonic acid (XXV) gives a not very high yield (~4%) [87]:



(XXV) (XXVI)

Compounds $ArSO_2X$ other than sulphonic acids are able to undergo nucleophilic photosubstitution. This has been shown for derivatives of sulphanilic acid and related compounds, such as *p*-aminobenzenesulphonamide (XXVIIa), *p*-trifluoromethylsulphonylaniline (XXVIIb), and *p*-methylsulphonylaniline (XXVIIc) subjected to photolysis in aqueous

solutions containing cyanide, nitrite, and thiocyanate ions [87]:

$$p\text{-}NH_2C_6H_4SO_2X \xrightarrow[H_2O]{h\nu,Nu^-} p\text{-}NH_2C_6H_4Nu + PhNH_2$$
(XXVIIa-c) (XXVIII) (III)

X=NH_2 (a), CF_3 (b), CH_3 (c); Nu=CN, NO_2, SCN .

The action of the cyanide ion gives 60–65% yields of photosubstituted products from compounds (XXVIIa) and (XXVIIc), but only 12–15% from (XXVIIb) and benzenesulphonamide. Compounds (XXVIIa) and (XXVIIc) react less vigorously with the nitrite ion: yields of the corresponding nitro-compounds are 2–4%. A still lower yield is obtained from (XXVIIa) with sodium thiocyanate. The photoreaction of (XXVIIc) with sodium methoxide in methanol forms only traces of *p*-anisidine (XXIX), the main product being aniline (III):

$$p\text{-}NH_2C_6H_4SO_2Me \xrightarrow{h\nu,MeOH,MeONa} p\text{-}NH_2C_6H_4OMe + (III) .$$
(XXVIIc) (XXIX)

Attempts to replace the SO_2X group by a fluorine atom by exposing aqueous solutions of (XXVIIa) and (XXVIIc) containing fluoride ions were unsuccessful. The relative unreactivity of the fluoride ion in photosubstitutions was attributed [87] to its high redox potential.

In all cases of photolysis of the compounds (XXVIIa)–(XXVIIc) photoelimination of the SO_2X group, leading to formation of aniline, competes with photosubstitution. As with halogenobenzenes, the latter process itself is activated by electron-donor substituents in the aromatic ring. The relative immobility of the SO_2X group on reaction with the nitrite ion is due to the low energies of the singlet and triplet levels of the latter, so that it can act not only as a nucleophilic reagent but also as an acceptor of the energy of excitation of the substrate.

As with sulphonic acids (see e.g. the photolysis of benzelesulphonic acid in aqueous solution, above) substitution of the SO_2X group (X ≠ OH) may begin with homolytic cleavage of the Ar–S bond. Thus *SS*-dimethyl-*N*-arenesulphonylsulphoximines (XXX) on exposure in aromatic hydrocarbons to light of wavelength 254 nm generate radicals which arylate the solvent [88]:

$$ArSO_2N{=}\overset{\overset{O}{\uparrow}}{S}Me_2 \xrightarrow{h\nu,C_6H_6} [Ar^\cdot] \xrightarrow{C_6H_6} ArPh .$$
(XXX) (XXXI)

Diaryl sulphones (XXXII) behave similarly on photolysis in benzene. The processes involved can be represented by the scheme [89]

$$ArSO_2Ar \xrightarrow[C_6H_6]{h\nu\,(254\ nm)} Ar^\cdot + ArSO_2^\cdot ,$$
(XXXII)

$$Ar^\cdot + C_6H_6 \longrightarrow Ar\text{-}C_6H_6^\cdot ,$$

$$Ar\text{-}C_6H_6^\cdot + ArSO_2^\cdot \text{ or } Ar^\cdot \longrightarrow ArC_6H_5 + ArSO_2H \text{ or } ArH ,$$

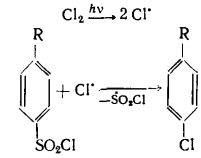
$$ArSO_2^\cdot + C_6H_6 \longrightarrow ArSO_2\text{-}C_6H_6^\cdot ,$$

$$ArSO_2\text{-}C_6H_6^\cdot + ArSO_2^\cdot \text{ or } Ar^\cdot \longrightarrow ArSO_2C_6H_5 + ArSO_2H \text{ or } ArH .$$

The suggested mechanism is supported by data on the distribution of carbon-14 in the products of photolysis of a labelled model compound—diphenyl sulphone [90].

Another type of radical photosubstitution of the SO_2X group is also possible, when the reagent—not the $ArSO_2X$ molecule—is excited, and forms radical species on photodissociation. This occurs when benzenesulphonyl and *p*-bromobenzenesulphonyl chlorides (XXXIIIa) and (XXXIIIb) in carbon tetrachloride containing excess of chlorine are exposed to the light from a tungsten lamp. The chlorosulphonyl group is replaced by a chlorine atom, and in (XXXIIIb) the bromine atom is also exchanged, the yields being 97% [91]:

$$Cl_2 \xrightarrow{h\nu} 2\,Cl^\cdot$$



(XXXIII a, b) (XXXIV a, b) .

$$^\cdot SO_2Cl \rightarrow SO_2 + {}^\cdot Cl$$

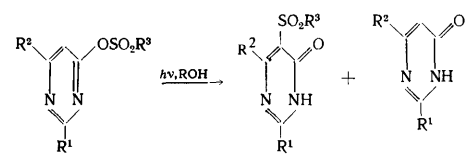
R=H (a), Br (b)

Phenyl and methyl benzenesulphonates do not undergo this reaction, but diphenyl sulphone (XXXV) gives a quantitative yield of chlorobenzene (XXXIVa) [91]:

$$Cl_2 \xrightarrow{h\nu} 2\,{}^\cdot Cl$$
$$PhSO_2Ph + {}^\cdot Cl \rightarrow PhCl + PhSO_2^\cdot$$
(XXXV) (XXXIVa)
$$PhSO_2^\cdot + Cl_2 \rightarrow PhSO_2Cl + {}^\cdot Cl$$
$$PhSO_2^\cdot \rightarrow Ph^\cdot + SO_2$$
$$Ph^\cdot + Cl_2 \rightarrow PhCl + {}^\cdot Cl$$
(XXXIVa) .

We have been discussing photochemical reactions of compounds $ArSO_2X$ in which the sulphur-containing group is either eliminated or replaced by another group, i.e. processes involving rupture of the Ar–S bond. These reactions have been most thoroughly investigated in the compounds considered. Nevertheless, we cannot disregard the considerably less studied but quite numerous photoprocesses of aromatic sulphonyl compounds $ArSO_2X$ in which the S–X bond is broken by the action of light, which leads to rearrangement or to stabilisation of the residue of the substrate molecule by interaction with the solvent (reagent).

Certain arenesulphonic esters [93,94] are arenesulphonamides [95] tend to undergo light-induced rearrangements like the Fries photorearrangement [92]. Thus exposure of 5-unsubstituted 2-dialkylaminopyrimid-4-yl arenesulphonates (XXXVI) in alcohols to the far ultraviolet (254 nm) converts them into 20–30% yields of the 5-arylsulphonyl-2-dialkylamino-4-hydroxypyrimidines (XXXVII) accompanied by small quantities of the 2-dialkylamino-4-hydroxypyrimidines (XXXVIII):

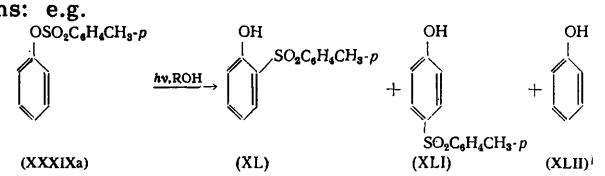


(XXXVI) (XXXVII) (XXXVIII)

R^1=NMe_2, morpholino, pyrrolidino, piperidino;
R^2 = H, Me; R^3=C_6H_5, *p*-MeC_6H_4, *p*-BrC_6H_4, *p*-ClC_6H_4, 2,5-$Me_2C_6H_3$

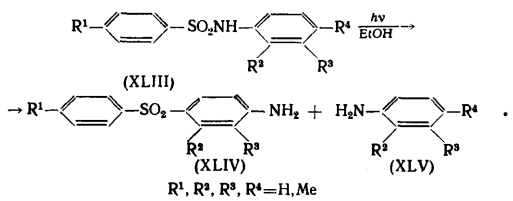
Phenyl and 1-naphthyl toluene-*p*-sulphonates (XXXIXa) and

(XXXIXb) undergo photorearrangement under similar conditions: e.g.



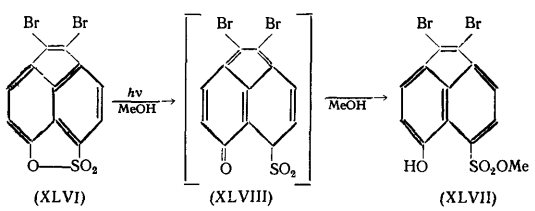
The reaction is assumed [96] to result from $\pi\pi^*$-excitation of the phenolic portion of the ester molecule.

Arenesulphonamides (XLIII) are converted photochemically into *p*-arylsulphonylarylamines (XLIV) in 6–25% yield and primary aromatic amines (XLV) in 25–70% yield:



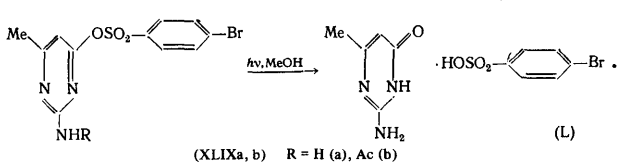
The relatively low yields of rearranged products are explained [95] by filtration of the light by the resulting sulphones (XLIV) and by unidentified coloured by-products of the reaction.

The acenaphthene sultone (XLVI), on illumination in methanol through a Pyrex filter, is converted into the corresponding methyl sulphonate (XLVII) [97] with intermediate formation of the sulphene (XLVIII):

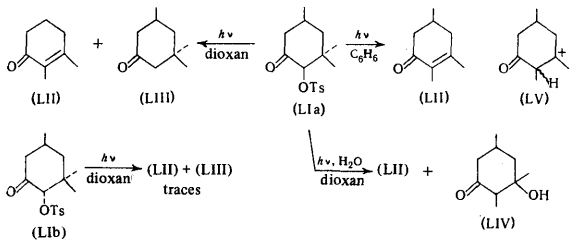


A singlet excited state of (XLVI) is assumed to take part in the photoreaction, but no strict proof of this is given.

In several cases light detaches the ester group from arenesulphonates, e.g. from 2-aminopyrimid-4-yl and 2-acetamidopyrimid-4-yl *p*-bromobenzenesulphonates (XLIXa) and (XLIXb) in ethanol. Instead of rearrangement (see above) a salt (L) of 2-amino-4-hydroxypyrimidine and the sulphonic acid is formed [93]:



Photoelimination occurs stereospecifically in the case of oxocycloalkyl toluene-*p*-sulphonates [98]. Thus exposure of the *cis*-isomer (LIa) in benzene forms an unsaturated ketone (LII), in dioxan a mixture (4 : 1) of (LII) and (LIII), and in aqueous dioxan the ketone (LII) and the β-hydroxy-ketone (LIV); the *trans*-isomer (LIb) in more stable, forming small quantities of the ketones (LII) and (LIII) (1 : 1) only on prolonged photolysis:



Photoreaction evidently requires a sterically accessible conformation of the carbonyl group and the $C_{(\alpha)}$–O bond, which is present in the ester (LIa) but not in its isomer (LIb). The $n\pi^*$ state of these ketones is regarded as reactive. Formation of the αβ-unsaturated ketone (LII) is explained by production of the cation (LV) by heterolytic cleavage of the C–O bond followed by migration of a methyl group and deprotonation of the cation [98].

In contrast to the long known de-O-tosylation of toluene-*p*-sulphonates of sugars by catalytic reduction, it has recently been suggested that this should be effected photochemically in methanolic sodium methoxide (in an inert gas) [99]. The corresponding sugars are formed in yields of 90% or more and, what is especially important, the photoreaction is not complicated by secondary processes, as occurs in the dark reaction.

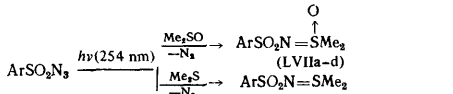
Photochemical cleavage of the sulphur–nitrogen bond (–SO_2NH–) in sulphonylated amino-acids and peptides might also have found practical application [100]. Unfortunately, however, the yields are not yet high enough for this photoreaction to be a serious competitor to the deblocking of tosylated amino-acids achieved in dark chemistry. This is due to the secondary processes of photodecarboxylation and photodeamination, and also to the photodegradation of certain unstable amino-acids (e.g. tryptophan).

We conclude this Section by considering photoreactions of aromatic sulphonyl compounds that do not affect the Ar–S and S–X bonds but involve cleavage of bonds in the X fragment of the molecule. Considerable interest has been taken in reactions of sulphonyl azides, which resemble aryl azides in photochemical behaviour, also being capable of breaking down with evolution of molecular nitrogen and formation of nitrenes—isoelectronic analogues of carbenes—on exposure to light. Like the latter, nitrenes are able to exist in singlet and triplet states $ArSO_2\ddot{N}$ and $ArSO_2\ddot{N}\cdot$. Electron spin resonance investigations have shown that the photolysis of benzenesulphonyl and toluene-*p*-sulphonyl azides (LVIa) and (LVIb) in matrices [101–103] at 77 °C yields the corresponding nitrenes in a triplet ground or excited state (the latter readily attainable by thermal activation).

The photochemical reactions of arenesulphonyl azides are usually regarded as those in which the photolytically generated nitrene undergoes rearrangement or else interacts with the solvent or the reagent. However, a critical attitude has recently been adopted towards this approach, on the assumption that in certain processes elimination of nitrogen is not the primary step (see below). The photolysis of sulphonyl azides in aprotic solvents (benzene, cyclohexane, thiophen, pyridine, etc.) usually yields insoluble resinous or polymeric products; intermediate formation of nitrenes is almost impossible to demonstrate [104,105].

Exposure of arenesulphonyl azides (LVIa–d) in dimethyl

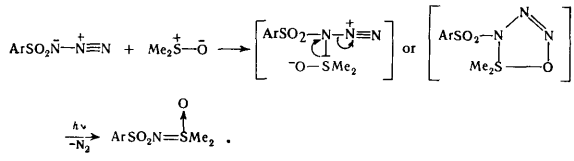
sulphoxide and in dimethyl sulphide produces *N*-sulphonylsulphoximines (LVIIa–d) (15–50%) and *N*-sulphonylsulphidimines (LVIIIa–d) (48–55%) respectively [104]:



(LVIIa–d) (LVIIIa–d)

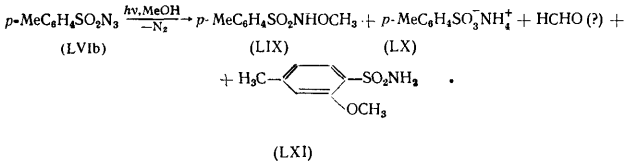
Ar=C_6H_5 (a), *p*-MeC_6H_4 (b), *p*-$NO_2C_6H_4$ (c), *p*-$MeOC_6H_4$ (d).

Whereas a mechanism of intermediate formation of nitrenes is alone assumed for the reaction with dimethyl sulphide, dimethyl sulphoxide also offers the possibility of complex formation between sulphonyl azides and the solvent (DMSO) acting as an electrophile, with expulsion of a nitrogen molecule on excitation of the complex:



The readily occurring photoreactions of sulphonyl azides in alcohols yield various compounds, which can be regarded formally as products of the insertion of nitrenes in the alcohol molecules, reduction of the nitrenes by detachment of a hydrogen atom, and the Curtius rearrangement [104–106]. It is especially difficult to determine in these photoreactions whether or not nitrenes are formed as intermediates.

The photolysis of toluene-*p*-sulphonyl azide (LVIb) in methanol gives a 44% yield of O-methyl-*N*-toluene-*p*-sulphonylhydroxylamine (LIX) and small quantities of ammonium toluene-*p*-sulphonate (LX), a volatile substance (probably formaldehyde), and 2-methoxy-4-methylbenzenesulphonamide (LXI)[104]:

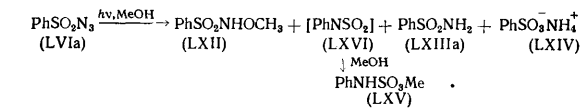


(LVIb) (LIX) (LX)

(LXI)

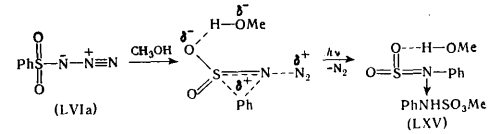
This process has an induction period: evolution of nitrogen begins after fairly long illumination of the reaction solution. If the solution is kept in the dark, however, reaction begins from the moment of exposure.

A more rigorous investigation of this reaction on benzenesulphonyl azide (LVIa) showed [105,107] that methyl *N*-phenylsulphamate (LXV) is formed together with the compounds (LXII)–(LXIV) (in yields respectively of 15, 4.5, and 8%):



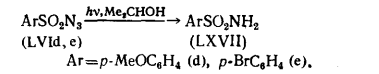
(LVIa) (LXII) (LXVI) (LXIIIa) (LXIV) (LXV)

Compound (LXV) can be assumed to result from rearrangement of the corresponding nitrene into *N*-sulphurylaniline (LXVI) followed by reaction with methanol. An alternative mechanism suggested involves protonation of the initial sulphonyl azide (formation of a hydrogen bond) and the photoinduced concerted rearrangement of such reactive complex with loss of a nitrogen molecule:



(LVIa) (LXV)

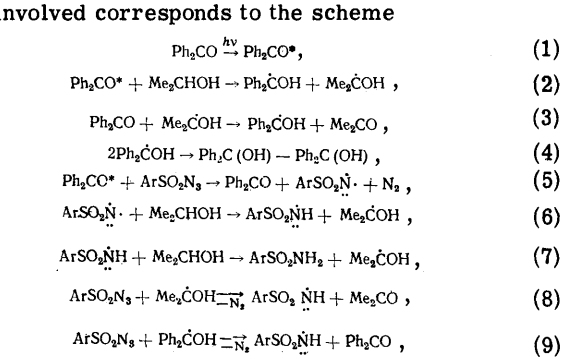
The photolysis of arenesulphonyl azides (LVId) and (LVIe) in propan-2-ol (excited by 254 or 365 nm in the presence of a sensitiser—benzophenone), in contrast to the above processes, gives only the corresponding arenesulphonamides (LXVII) in 85–95% yield [106]:



(LVId, e) (LXVII)

Ar=*p*-$MeOC_6H_4$ (d), *p*-BrC_6H_4 (e).

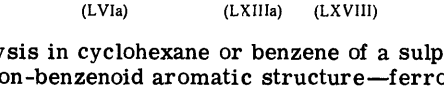
In this case detachment of a hydrogen atom predominates substantially over rearrangement, perhaps becuase of the greater mobility of the hydrogen atom attached to the carbinol carbon of the secondary alcohol. The radical-chain process involved corresponds to the scheme



(1)–(9)

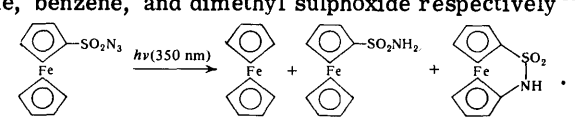
with the possible exclusion of Eqn. (2) or Eqns. (5) and (6).

Free-radical decomposition takes place also in the photolysis of benzenesulphonyl azide (LVIa) in benzenethiol, when benzenesulphonamide (LXIIIa) and diphenyl disulphide (LXVIII) are obtained [108]:



(LVIa) (LXIIIa) (LXVIII)

Photolysis in cyclohexane or benzene of a sulphonyl azide of non-benzenoid aromatic structure—ferrocenesulphonyl azide (LXIX)—results in ferrocene (LXX), ferrocenesulphonamide (LXXI), and a cyclisation product (LXXII), the last in yields of 13.3%, 67%, and 0 in cyclohexane, benzene, and dimethyl sulphoxide respectively [109]:

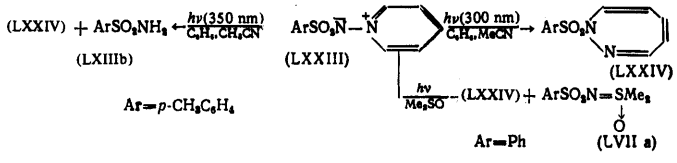


(LXIX) (LXX) (LXXI) (LXXII)

Formation of the free nitrene is postulated [109] on photolysis; cyclisation is probably a singlet reaction, since the yield of (LXXII) is not diminished by the presence of oxygen or quinol.

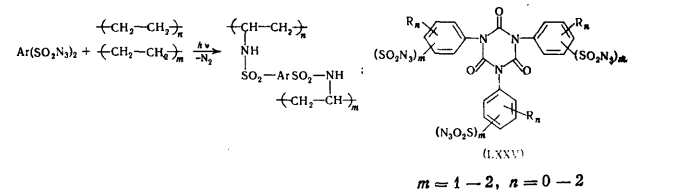
Formation of nitrenes was expected also when pyridinium ylids (LXXIII) were eliminated [110]. However, photolysis of the ylid (LXXIII: Ar = C_6H_5) in a mixture of benzene and acetonitrile by filtered radiation of wavelength 300 nm gave the compound (LXXIV) in 76% yield; compounds

which might have been formed from nitrenes (benzenesulphonamide, *N*-phenylsulphonylazepine) were not detected; in dimethyl sulphoxide the yield of (LXXIV) falls to 12%, and the sulphoximine (LVIIa) is formed in 40% yield:



Photolysis of the ylid (LXXIII: Ar = *p*-$CH_3C_6H_4$) by wavelength 350 nm resulted in low yields of the diazepine (LXXIV: Ar = *p*-$CH_3C_6H_4$) and toluene-*p*-sulphonamide (LXIIIb) (2:1). Thus under certain conditions of photolysis the stable pyridinium ylids of type (LXXIII) are able to produce sulphonylnitrenes.

We note in conclusion the practical value of sulphonyl azides as cross-linking agents for several polymeric materials. This exploits the property exhibited by sulphonylnitrenes formed on exposure of entering into carbon-hydrogen and oxygen–hydrogen bonds: e.g.



Several di- and poly-sulphonyl azides, in particular tris-azidosulphonylphenylhexahydrotrioxo-1,2,5-triazines (LXXV), find application in photographic resins [111-113].

IV. PHOTOREACTIONS NOT INVOLVING THE SO_2X SUBSTITUENT

The chief reactions of this type involve photoreduction of the carbonyl group in compounds containing an SO_2X substituent. The most thoroughly studied among them are the photochemical dehydrogenation of organic compounds by anthraquinonesulphonic acids and the oxidation by the latter of inorganic anions. An impetus to such interest in the photodehydrogenating power of anthraquinone and its sulphonic acids was provided by research on the photodegradation of natural and artificial fibres sensitised by anthraquinone vat dyes [114-126].

The mechanism of the photodehydrogenation of alcohols, which has been studied in detail, is at present regarded as

$$AS \xrightarrow{h\nu} AS^*$$

$$AS^* + R^1R^2CHOH \rightarrow ASH^{\cdot} + R^1R^2\dot{C}OH$$

$$R^1R^2\dot{C}OH + AS \rightarrow R^1R^2CO + ASH^{\cdot} \qquad ASH^{\cdot} + O_2 \rightarrow AS + HO_2^{\cdot}$$

$$2\,ASH^{\cdot} \rightarrow AS + ASH_2 \qquad R^1R^2\dot{C}OH + O_2 \rightarrow R^1R^2CO + HO_2^{\cdot}$$

$$ASH_2 + O_2 \rightarrow H_2O_2 + AS$$

$$2\,HO_2^{\cdot} \rightarrow H_2O_2 + O_2 .$$

absent oxygen present

The hydrogen atom is abstracted from the carbinol carbon atom by an excited anthraquinonesulphonate molecule (AS*) with formation of the semiquinone (ASH$^{\cdot}$) and the radical $^{\cdot}CR^1R^2OH$. A second hydrogen atom is detached, from the hydroxy-group of the radical, this time by an unexcited substrate molecule (AS), with formation of a second semiquinone molecule (ASH$^{\cdot}$) (per light quantum absorbed) and the ketone or aldehyde respectively. The product of complete reduction of the quinone (AS)—the anthraquinolsulphonic acid (ASH_2)—is obtained by disproportionation of the semiquinones (ASH$^{\cdot}$). If oxygen is present in the reaction mixture, it oxidises the semiquinone (ASH$^{\cdot}$) and the anthraquinol (ASH_2) to the initial quinone (AS), so that the final reaction products are in effect only the ketone or aldehyde. For this reason the process has been termed a "photosensitised oxidation of alcohols". It can quite rightly be termed also "photocatalytic" or—more correctly, in the Reviewers' opinion— a "chemically sensitised process", since the role of the quinone is not to transfer energy to the carbinol radical but, as an excited molecule, to interact chemically with the alcohol.

Table 1. Ratio of rate constant of detachment of a hydrogen atom to rate constant of all other processes effecting deactivation of excited states of anthraquinone-2-sulphonate k_1/k_0 during photodehydrogenation [116,117].

Compound to be dehydrogenated	k_1/k_0	Compound to be dehydrogenated	k_1/k_0
Methanol	0.054	Ethane-1,2-diol	0.258
Ethanol	0.445	Propane-1,2-diol	0.56
Propan-1-ol	0.682	Propane-1,2,3-triol	0.374
Propan-2-ol	0.921	Cyclohexanol	2.31
Butan-1-ol	0.952	Diethyl ether	2.14
Butan-2-ol	1.270	Di-isopropyl ether	1.80
2-Methylpropan-2-ol	0.01	Acetone	0

Besides alcohols (monohydric and polyhydric), ethers and ketones can also be photodehydrogenated by sulphonated anthraquinones. The comparative reactivities of all these compounds towards photodehydrogenation has been studied [116,117] as the ratio of the photodehydrogenation rate constant to the total rate constant of the other processes by which the excited state of the substrate is deactivated (Table 1). The reactivity of alcohols towards photodehydrogenation by anthraquinone-2-sulphonic acid (XII) increases with the length and the degree of branching of the hydrocarbon chain, which is attributed to increasing mobility of the hydrogen atom attached to the carbinol carbon atom resulting from increase of the positive inductive effect of the alkyl group in the alcohol molecule [116]. The absolute rate constants of detachment of the hydrogen atom from certain alcohols, measured by flash photolysis, are around $10^6\ M^{-1}\ s^{-1}$. [120,127]

The above reactivity sequence of alcohols towards photodehydrogenation by anthraquinone-2-sulphonic acid (XII) indicates that the primary photochemical step consists in detachment of a hydrogen atom, not in transfer of an electron. An energetic assessment of photodehydrogenation leads to the same conclusion, showing that energies of excitation of anthraquinonesulphonic acids are insufficient to abstract an electron from an alcohol molecule [127]. The above results apply to alcoholic or neutral aqueous–alcoholic solution. In alkaline aqueous–alcoholic media and in alcoholic solutions of the corresponding sodium alkoxide, however, electron transfer from the alkoxide ion to the excited sulphonic acid

$$AS^* + RO^- \rightarrow AS^{\cdot-} + RO^{\cdot}$$

predominates. The possibility of this process has been confirmed [128,129] by a detailed study of the photoreduction

of sulphonated anthraquinones by electronic and electron spin resonance (e.s.r.) spectroscopy.

In ethers a hydrogen atom is abstracted from a carbon atom forming the ether bond. Increase in the length and the degree of branching of the alkyl groups diminishes the reactivity of the ether owing to the shielding effect [117].

The simplest ketone (acetone) shows little tendency to undergo photo-oxidation by anthraquinonesulphonic acids, but the rate of the process is substantially larger in alkaline aqueous solutions. This can be attributed either to reaction of acetone as the enolic form [117] $CH_3.CH(OH):CH_2$ or to involvement of the hydroxide ion in the reaction (see below).

Alcohols (and other organic compounds) undergo considerably less photo-oxidation in the presence of 1-sulphonates than of 2-sulphonates of anthraquinone (Table 2), so that less study has been made of the behaviour of the 1-isomers in this process. Thus the introduction of a sulpho-group into the anthraquinone molecule, which might be expected to influence only the solubility in organic and aqueous media, leads to substantial differences in the photodehydrogenating power of the quinonoid group depending on the position of the sulpho-group.

Table 2. Quantum efficiencies of the formation of anthraquinole in the photodehydrogenation of propan-2-ol [122].

Sulphonated anthraquinone	Quantum efficiency	Solvent
Anthraquinone	0.81	benzene–propan-2-ol (4 : 1)
2-Sulphonated	1.06	propan-2-ol
2,6-Disulphonated	1.07	
2,7-Disulphonated	1.14	
1-Sulphonated	0.05	
1,5-Disulphonated	0.015	

For a long time the spectral sensitivity of the photoreduction of anthraquinone and its sulpho-derivatives remained an unsolved problem. Investigation of anthraquinone-1-sulphonic acids in alkaline aqueous–alcoholic solutions merely showed [128] that the quantum efficiency of photoreduction was the same throughout the range of absorption of the substrate, whence it may be concluded that conversion to a reactive state with higher energy levels takes place with equal probability.

The involvement of the triplet state of anthraquinone [122] and its sulphonated derivatives [127] in the photodehydrogenation of alcohols has been shown by triplet–triplet energy transfer. Not only the 2-sulphonates, which actively dehydrogenate alcohols, but also the less active 1-isomers take part in this process in an excited triplet state [126]. Of the two possible triplet states of anthraquinones only the $n\pi^*$ state possesses dehydrogenating power, when excitation is localised in a carbonyl group, and a hydrogen atom may be abstracted by a radical-like oxygen atom. The $T_{\pi\pi^*}$ state of the substrate, characterised by delocalisation of the excitation energy in the π-electron system of the molecule, is inactive in these processes. Such an approach makes it obvious that substances in which the lowest triple level is an $n\pi^*$ level are good acceptors of hydrogen [130,131]. With compounds which hardly dehydrogenate alcohols at all—hydroxy- and amino-anthraquinones (and also anthraquinonesulphonic acids containing these electron-donor groups)—the energy levels are inverted, and the unreactive $T_{\pi\pi^*}$ state becomes the lowest [55]. Certain authors attribute the low reactivity of anthraquinone-1-sulphonates (compared with the 2-isomers) in photodehydrogenation to the low probability of the interconversion $S \rightarrow T$: with the 2-sulpho-derivatives this probability is approximately unity [132].

Anthraquinonesulphonic acids can be reduced photochemically not only by organic compounds but also by inorganic anions, e.g. hydroxide ions [133–137]. The reaction entails in effect the transfer of an electron from the ion to an excited acid molecule with formation of a hydroxyl radical and a radical-anion ($AS^{\cdot -}$), the latter being fairly stable in alkaline media. These radical-anions have been recorded by e.s.r. [133] (for the structure of the spectra see Ref. 124) and by electronic [137] spectroscopy. Use of these methods to study the kinetics of formation of the radical-ions as a function of the hydroxide-ion concentration confirmed [133,137] that the hydroxide ion—not a water molecule, as postulated previously [135]—is actually the electron donor:

$$AS^* + {}^-OH \rightarrow AS^{\dot{-}} + {}^{\cdot}OH \ .$$

The radical-ions ($AS^{\cdot -}$) interact vigorously with oxygen

$$AS^{\dot{-}} + O_2 \rightarrow AS + O_2^{\dot{-}},$$

with a rate constant $k = \simeq 10^8\ M^{-1}\ s^{-1}$. Hence accumulation of these radical-ions is observed only in deaerated media [121].

Alkaline solutions contain hardly any semiquinone ($ASH^{\cdot}$)—the protonated form of the radical-anion ($AS^{\cdot -}$)—since the pK is small (e.g. 2.3–3.2 for the radical-anion obtained from anthraquinone-2,6-disulphonic acid [127,138]). In contrast to the semiquinone, whose disproportionation rate constant lies in the range 10^8–$10^9\ M^{-1}\ s^{-1}$, the ionised form ($AS^{\cdot -}$) disproportionates far more slowly ($k_{dispr} < 10^2\ M^{-1}\ s^{-1}$) [127]. In alkaline solutions, therefore, the equilibrium

$$2AS^{\dot{-}} \rightleftarrows AS^- + AS$$

is displaced to the left, which enables a nearly quantitative yield of the radical-anions to be obtained.

The formation of hydroxyl radicals in these reactions could not be detected by physical methods, because of their great reactivity and the frequent ambiguity of their identification by characteristic reactions [136]. Direct evidence of the photochemical generation of hydroxyl radicals in alkaline aqueous solutions of anthraquinonesulphonic acids was the detection of $CO_3^{\dot{-}}$ radical-anions in the reaction mixtures on illumination by flash photolysis in the presence of added carbonate ions. This radical-ion is formed by the interaction of a hydroxyl radical and a carbonate ion [134]:

$$HO^{\cdot} + CO_3^{2-} \rightarrow HO^- + CO_3^{\dot{-}} \ .$$

The Stern–Volmer relation gave the value $k_T\tau \simeq 2000$–$3000\ M^{-1}$ for the photoreaction of the hydroxyl ion with anthraquinone-2,6-disulphonic acid (quenched by iodide, thiocyanate, thiosulphate, and hexacyanoferrate(II) ions) [132]. From this it was found that the lifetime of the reactive state of the substrate lay within the limits $\tau = 10^{-7}$–10^{-5} s depending on the value of $k_T = 10^8$–$10^{10}\ M^{-1}\ s^{-1}$ used in the calculations. Such a lifetime is more typical of a T than of an S state, from which it was concluded that a triplet state of the anthraquinonesulphonates is active in the present process as in photodehydrogenation. Flash photolysis has since been used to record the triplet states of anthraquinone-2-sulphonates and determine their absorption spectra (λ_{max} = 480–500 nm). Their deactivation

obeys a first-order kinetic equation (k_{des} = 34 000 s^{-1} for anthraquinone-2,6-disulphonic acid at pH 6.5). Deactivation is accelerated considerably by the presence of an acceptor of triplet energy (e.g. anthracene-1-sulphonic acid) because of efficient energy transfer. A similar effect is produced by the introduction of electron donors (hydroxide and carbonate ions): the rate constants of their reaction with excited anthraquinone-2,6-disulphonic acid are respectively 7.1×10^6 and 1.8×10^6 M^{-1} s^{-1}. These results finally confirmed that a triplet state of anthraquinone-2-sulphonic acids was involved in electron transfer [127].

The quantum efficiencies of the photoreduction of various anthraquinone derivatives have been compared for the photoreaction with the carbonate ion [127]. Efficiencies of around unit are obtained with mono- and di-sulphonic acids containing a 2-sulpho-group; with anthraquinone-1-sulphonic acid and hydroxyanthraquinones the quantum efficiencies are respectively 0.32 and 0. Hence compounds whose lowest triplet level is an $n\pi^*$ level are active in processes involving the phototransfer of an electron, as in photodehydrogenation.

The fairly high quantum efficiencies of photoreduction of the anthraquinone-1-sulphonate (XIa) by the carbonate ion in aqueous solution [127] and the limiting quantum efficiency of its photoreduction in a methanolic solution of sodium methoxide (Φ_{lim} = 0.40 [129]) indicate that in these cases $\Phi_{ST} \geqslant 0.3$ for 1-sulphoanthraquinone. Thus the above hypothesis, that the low reactivity of anthraquinone-1-sulphonic acids towards photodehydrogenation is due solely to the extraordinarily low probability of their occupying a triplet level, must be regarded as questionable. However, data are still lacking that would enable us to find the true reason for the low photodehydrogenating activity of anthraquinone-1-sulphonic acids in comparison with the 2-isomers.

Excited anthraquinonesulphonic acids are photoreduced not only by hydroxide and carbonate ions but also by chloride, sulphate, and thiocyanate ions. They are not reduced by fluoride, chlorate, metabisulphite, and bromate ions. This sequence has enabled the redox potential of the $AS_{T,n\pi^*}/AS^{\cdot -}$ pair to be estimated: it lies between those of the pairs $Cl^{\cdot}/Cl^-$ and $F^{\cdot}/F^-$ (2.55 and 3.6 eV) [127].

Radical-anions of sulphonated anthraquinones are formed in low yields on flash photolysis in neutral aqueous solutions containing bromide or iodide ions. Two competing processes—electron transfer and physical quenching—are assumed to occur in the exciplex of the halide ion and the sulphoanthraquinone molecule in an excited triplet state:

$$AS \xrightarrow{h\nu} AS^* \xrightarrow{X^{-n}} [AS \ldots X^{-n}]^* ,$$
$$X^{-n} + AS \xleftarrow{k_T} [AS \ldots X^{-n}]^* \xrightarrow{k_P} \dot{X}^{-(n-1)} + AS^{\cdot -} ,$$

where $k_T \gg k_P$ for iodide and bromide ions, but $k_P \gg k_T$ for carbonate, sulphate, and other ions [127].

However, the above scheme probably does not fully represent the processes occurring in the reaction system. Thus a study of the photoreduction of sulphonated anthraquinones in alkaline aqueous and aqueous–alcoholic solutions revealed regularities that cannot be explained by this scheme. Whereas with iodide ions the slowing down of the reaction conforms closely with simple Stern–Volmer equation, with chloride and bromide ions such conformity is observed only at low concentrations, and increase in the chloride-ion concentration is accompanied by an increase in reaction velocity right up to the original rate in the absence of quenching anions. These facts were explained on the hypothesis [129] that chloride ions are able to form a fairly stable charge-transfer complex with the unexcited anthraquinonesulphonic acid. Absorption of light by the complex leads to the appearance of radical-anions of the sulphonated anthraquinone. Quenching, however, occurs by interaction of a chloride ion with an excited anthraquinonesulphonate molecule:

$$AS_{fr.} + Hal^- \rightleftarrows [AS \ldots Hal^-] ,$$
$$AS_{fr.} \xrightarrow{h\nu} AS^*_{fr.} ,$$
$$AS^*_{fr.} \rightarrow AS_{fr.}$$
$$AS^*_{fr.} + Hal^- \rightarrow AS^{\cdot -} + Hal^{\cdot} ,$$
$$AS^*_{fr.} + X^- \rightarrow AS^{\cdot -} + X^{\cdot} ,$$
$$[AS \ldots Hal^-] \xrightarrow{h\nu} [AS \ldots Hal^-]^* ,$$
$$[AS \ldots Hal^-]^* \rightarrow [AS \ldots Hal^-] ,$$
$$[AS \ldots Hal^-]^* \rightarrow AS^{\cdot -} + Hal^{\cdot}$$
$$X = OH, OAlk .$$

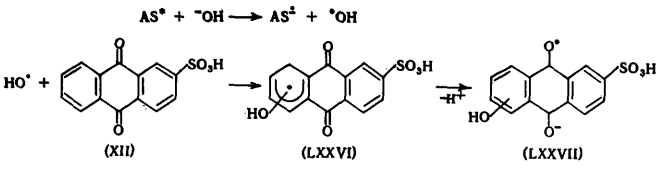
Calculation based on the kinetic scheme of photoreduction taking into account the above assumptions provides a qualitative explanation of the observed regularities [129].

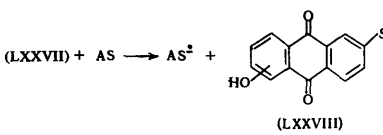
The forward (photochemical) electron-transfer reaction is always accompanied by the reverse (dark) reaction of radical-anions of sulphonated anthraquinones with products of the one-electron oxidation of inorganic ions. In some cases the rate constants of such reverse reactions are extremely large: e.g. $k = 10^9$ M^{-1} s^{-1} for the reaction [127]

$$AS^{\cdot -} + CO_3^{\cdot -} \rightarrow AS + CO_3^{2-}$$

The disappearance of $CO_3^{\cdot -}$ radical-ions after the flash is due solely to the above process, since they hardly interact at all among themselves or with the initial anthraquinonesulphonic acids. Under steady illumination their yield in solutions containing carbonate ions will be extremely small (even if the reaction is conducted under conditions such that the radical-anions ($AS^{\cdot -}$) are stable, i.e. do not disproportionate).

Sometimes the reverse reaction is comparatively slow, and the photochemical electron transfers from anions to excited sulphoanthraquinone molecules are then accompanied by secondary dark processes. This occurs in the photo-oxidation of hydroxide ions, for example, when the resulting hydroxyl radicals interact mainly with the initial sulphonated anthraquinone [137]. The hydroxyl radical is weakly electrophilic [139], so that it enters only the unsulphonated ring [132]. This gives the adduct (LXXVI) or the radical-anion (LXXVII), which are oxidised by the original quinone (AS) to the corresponding hydroxyanthraquinonesulphonates (LXXVIII):





(LXXVIII)

Hydroxylation actually takes place by a radical mechanism, which is confirmed by the diminished yield of hydroxy-derivatives (LXXVIII) on the introduction of acceptors of hydroxyl radicals into the reaction mass and by the fact that the same compounds are obtained by the action of Fenton's

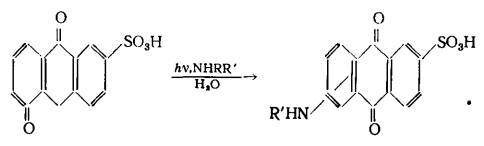
reagent on anthraquinonesulphonates as by the photochemical reaction [135,136].

The position entered by the hydroxy-group depends on the pH: at pH = 7–12 the main products of the photoreaction are 6- and 7-hydroxyanthraquinone-2-sulphonates, and these are the sole products at pH > 12; in neutral solutions hydroxylation occurs both at positions 6 and 7 and at positions 5 and 8.[136,139] Since hydroxyl radicals are able to undergo the dissociation

$$\cdot OH \rightleftarrows O^{\cdot -} + H^+,$$

with pK = 11.9,[140] the formation of different products is probably due to different hydroxylating agents according to the pH—the hydroxyl radical in neutral and weakly alkaline media and the oxide radical-anion $O^{\cdot -}$ in strongly alkaline media. All these assumptions require experimental confirmation, of course, but nevertheless the selective addition of such active radicals as these is a noteworthy fact.

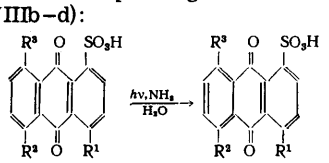
Not only anthraquinonesulphonates but also other compounds added to the solutions to be illuminated can be hydroxylated in this way. For example, phenol was obtained on the addition of benzene, which was also evidence of the formation of a hydroxyl radical in the photoreaction of the hydroxide ion with anthraquinonesulphonic acid [134]. When photohydroxylation takes place in the presence of an oxidant (molecular oxygen or potassium hexacyanoferrate(III) [133], the oxidation of hydroxide ions to hydroxyl radicals will be a cyclic process, so that the reaction may evidently be of value for the preparation of aromatic hydroxy-derivatives, especially as under certain conditions addition of a hydroxyl radical is a directed process. The photolysis of aqueous–ammoniacal solutions of anthraquinone-2-sulphonic acids probably resembles photohydroxylation. The 2-sulphonic acid (XII) forms amino-, diamino-, and amino-hydroxy-derivatives (principally 6(or 7)-aminoanthraquinone-2-sulphonates (LXXIX: R′ = H)): i.e. as in the preceding process, the unsulphonated ring undergoes substitution (amination). Photolysis of an aqueous solution of the sulphonated quinone (XII) in the presence of hydrazine (which breaks down into amino-radicals on exposure to ultraviolet radiation [141]) yields the same aminoanthraquinonesulphonic acids (LXXIX: R′ = H) as does photolysis in the presence of ammonia. The photochemical reaction of methylamine with anthraquinone-2-sulphonic acid (XII) gives the methylamino-derivatives (LXXXIX: R′ = CH_3) [142]:



(XII) (LXXIX)

R = H, NH_2; R′ = H, CH_3

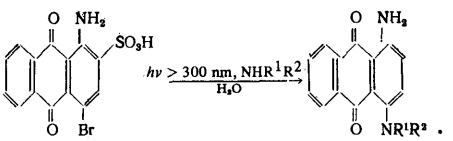
Not only hydrogen but also halogen can be replaced by an amino(or alkylamino)-group. Thus the photolysis of chloroanthraquinonesulphonic acids (XIe–g) in aqueous ammonia yields the corresponding aminoanthraquinonesulphonic acids (XVIIIb–d):



(XIe–g) (XVIIIb–d)

(XI : R^1, R^2, R^3 = H, Cl) (XVIII : R^1, R^3, R^3 = H, NH_2)

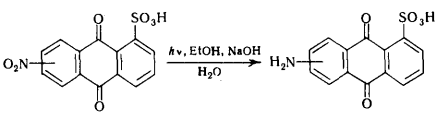
Although the yields are smaller (up to 6%), they are comparable with those of the simultaneously formed aminochloroanthraquinones (Section III) [74]. Bromine in the aminobromo-sulphonic acid (LXXX) is exchanged considerably better (probably because of the activating effect of the donor substituent). The process is conducted in aqueous solution; additions of aliphatic alcohols, dioxan, or acetonitrile increase significantly the yield of substitution products (LXXXI), which varies between 10% and 55%. Necessary conditions for the reaction are exposure to light of wavelength exceeding 300 nm and the presence of an oxidant (air or Fe^{3+} ions): only photodecomposition of the sulphonic acid (LXXX) takes place if these conditions are disrupted [143]:



(LXXX) (LXXXI)

R^1R^2NH=NH_3, $MeNH_2$ $EtNH_2$, $PrNH_2$, $BuNH_2$, piperidine

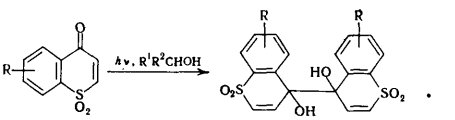
An amino-group can be formed also by photochemical reduction of a nitro-group. An attempt to effect the photodesulphonation of 5- and 8-nitroanthraquinone-1-sulphonic acids (XIl) and (XIm) in alkaline aqueous–ethanolic solution gave only a low yield (<5%) of the aminoanthraquinonesulphonic acids (XVIIIb) and (XVIIIc) [74]:



(XII, m) (XVIIIb, c)

Reduction of the nitro-group accompanied by loss of capacity for photodesulphonation is evidently due to the fact that the lowest reactive excited state of nitroanthraquinonesulphonic acids is the $T_{n\pi^*}$ level of the nitro-group, which is responsible for its photoreduction.

An example of photoreactions of non-quinonoid aromatic sulphonyl compounds that do not involve the SO_2X group is the photoreduction of 4-oxothiachroman 1,1-dioxides (LXXXII) in alcohols, when the yields of the pinacols (LXXXIII) reach 30%:



(LXXXII) (LXXXIII)

The electronic effect of the substituent is assumed to have little effect on the course of the process, with steric factors playing a considerably larger role [96].

The above account shows that the photochemistry of aromatic sulphonyl compounds is at present in an initial state of development. Future investigations of their photochemical reactions will undoubtedly provide answers to the problems examined in the present Review and to many others of importance not only for the present group of compounds but also for organic photochemistry in general.

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