Photoisomerization and Photodegradation of Metanilic Acid

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The photolysis of metanilic acid (**1**) as the sodium metanilate, through quartz under helium at λ = 254 nm leading to the isomeric anilinesulphonic acids (**2** and **3**) and aniline (**4**) has been studied in water. The effects of pH and solvent on products, the acid–base catalysis of the photoreaction (pH–product profile) and the effects of substrate concentration, radical scavenging, triplet sensitization and quenching studies are reported.

A mechanism involving a single triplet and a series of σ-complexes is proposed.

Thermal isomerization of orthanilic acid (**2**) to sulphanilic acid (**3**) in concentrated sulphuric acid at high temperatures was first reported almost one hundred years ago[1] and has been the subject of considerable study in recent times.[2,3] Metanilic acid (**1**) does not isomerize under similar conditions.

There are a number of reports on the photochemistry of sulphonic acids and sulphonates[4–10] and two major reaction pathways have been recognized for arenesulphonic acids or their sodium salts.[4,5,7] The primary photochemical process in aqueous solution appears to be C–S bond cleavage *via* the Π,Π^* excited state, leading to desulphonation and the formation of the corresponding aromatic hydrocarbon [eqn. (1)]. A competing process of desulphonylation leading to the formation of the corresponding phenol, or its quinonoid oxidation products, if oxygen is present, may also occur [eqn. (2)].

$$\mathrm{ArSO_3^-} \xrightarrow{h\nu} \mathrm{Ar^{\bullet}} + {}^{\bullet}\mathrm{SO_3^-} \qquad (1)$$

$$\mathrm{ArSO_3^-} \xrightarrow{h\nu} \mathrm{ArOSO_2^-} \longrightarrow \mathrm{ArO^-} + \mathrm{SO_2} \qquad (2)$$

Desulphonation proceeds *via* the excited triplet state and desulphonylation involves an initial rearrangement of the sulphonate to the isomeric sulphite possibily *via* an oxathiiran intermediate and a singlet excited state. We were not aware of any studies on the photochemistry of aminobenzenesulphonic acids and we decided therefore to examine the photochemistry of metanilic acid as a starting point.

Results and Discussion

Since the thermal rearrangements of the anilinesulphonic acids are acid catalysed it was decided to irradiate metanilic acid at a number of pH values, initially to probe the effect of acid or base on any photoreaction occurring. Figs. 1(*a*)–(*c*) show the UV spectral changes upon irradiation at λ = 254 nm of dilute aqueous metanilic acid solutions. The spectra of metanilic acid at pH 4.2 and 11.3 change markedly upon irradiation but the spectrum at pH 7.9 shows little change. From the isosbestic points observed in Figs. 1(*a*) and (*c*) the photoreaction appears to be quantitative, especially at pH 11.3. Also in view of the fact that there is little or no change in the UV spectrum at pH 7.9 [Fig. 1(*b*)], the reaction also appears to be subject to acid and base catalysis. Finally an aerated methanolic solution of metanilic acid showed considerably less spectral change than a degassed one. This is suggestive of substantial physical quenching of a triplet excited state which would be an intermediate in the photoreaction and also provides a forewarning as to the exclusion of oxygen in future irradiations.

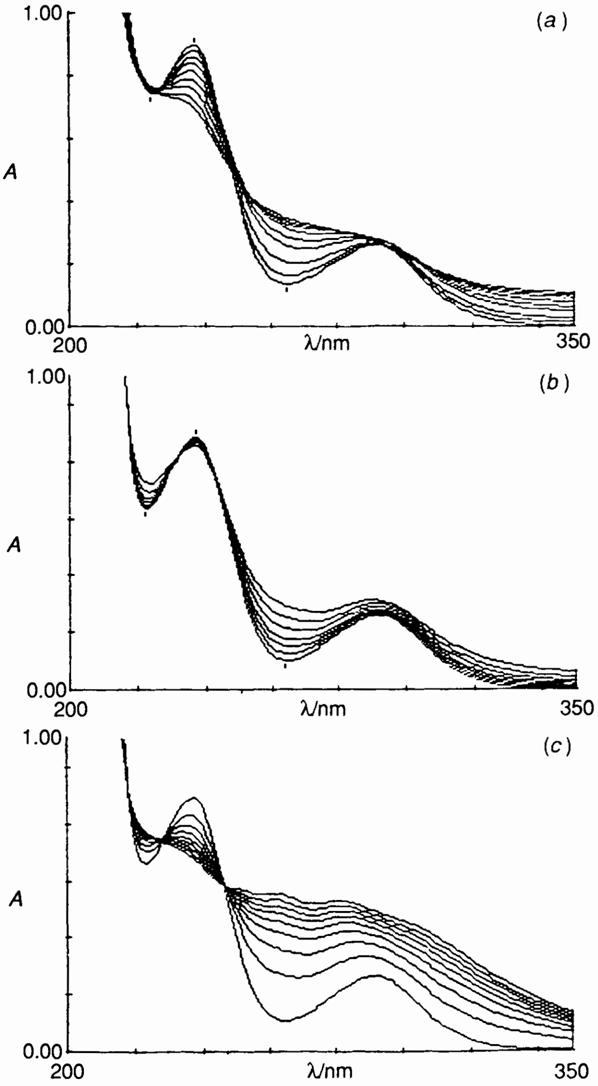


Fig. 1 Spectral changes of degassed aqueous solutions of metanilic acid at (*a*) pH 4.2, (*b*) 7.9 and (*c*) 11.3 with irradiation time at λ = 254 nm. Total irradiation time at each pH, *ca.* 80 s.

Product Study: Effect of pH *and Solvent.*—In view of the results obtained by UV monitoring above, metanilic acid (sodium salt) was irradiated pH 4.2 and 11.2 in both methanol and water under nitrogen. The resulting photolysis mixtures were analysed by reversed-phase HPLC to determine the product distribution and the effect of pH and solvent on this

Table 1 Effect of solvent and pH on product distribution[a,b]

pH	Solvent	Conversion (%)	Aniline (%)	Orthanilic acid (%)	Sulphanilic acid (%)	*ortho*/*para* Ratio	Aniline/(*o* + *p*)[c]
4.2	Water	13.6	46.5	13.5	34.7	0.39	0.96
	Methanol	20.5	37.2	15.6	39.3	0.40	0.68
11.2	Water	3.9	62.6	8.4	24.3	0.35	1.91
	Methanol	11.5	27.5	19.8	52.0	0.38	0.38

[a] Metanilic acid (0.01 mol dm^{-3}) with irradiation time of 1 min. [b] Yields (%) based on consumed starting material. [c] Ratio of yield of degradation product, aniline, to yield of isomerization products.

Table 2 Dependence of product yields[a,b] on general acid (NaH_2PO_4–Na_2HPO_4) concentration at pH 5.2

Conditions	Aniline	Orthanilic acid	Sulphanilic acid
$HClO_4$, 1.0 mol dm^{-3} NaCl	6.35	1.81	4.63
0.25[c]	6.41	2.34	5.82
0.50	6.43	2.80	7.02
0.75	6.60	3.23	8.07
1.00	6.47	3.21	8.11

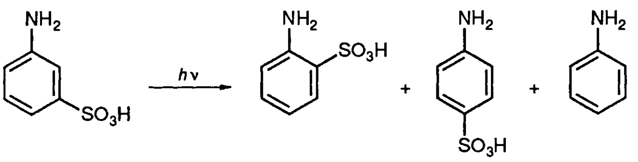
[a] Yields (/10^4 mol dm^{-3}) based on consumed starting material. [b] Metanilic acid (0.01 mol dm^{-3}) in water at constant ionic strength (1.0 mol dm^{-3}) after 1 min irradiation time. [c] Indicates concentration of NaH_2PO_4 (general acid) in the NaH_2PO_4–Na_2HPO_4 buffer.

Table 3 Dependence of product yields[a,b] on general acid (NaH_2PO_4–Na_2HPO_4) concentration at pH 6.1

Conditions	Aniline	Orthanilic acid	Sulphanilic acid
$HClO_4$, 1.0 mol dm^{-3} NaCl	4.81	1.35	3.24
0.25[c]	4.88	1.58	3.82
0.50	4.90	1.83	4.34
0.75	4.80	2.10	4.82
1.00	4.96	2.18	5.01

[a–c] As in Table 2.

distribution. The results obtained after irradiation of 0.01 mol dm^{-3} solutions for 1 min are presented in Table 1. Metanilic acid undergoes photoisomerization to sulphonic acids **2** and **3** and photodegrades to aniline **4** (Scheme 1) and it is apparent that changing the pH and solvent has a dramatic effect on the photoreaction. The use of methanol as solvent increases the per cent conversion and the overall yield of isomerization products. Two points are worthy of special note: (i) in all cases the mass balance was >90% indicating a clean reaction, and (ii) the apparent insensitivity of the *ortho*/*para* ratio to variation in pH and solvent suggests a tightly bound intermediate leading to the formation of the sulphonic acids, **2** and **3**.



1 **2** **3** **4**

Scheme 1

pH *Photoreaction Profile.*—The product yields for the photolysis of metanilic acid were measured as a function of medium pH at a substrate concentration of 0.01 mol dm^{-3} in water (Fig. 2). The photoreaction was found to be strongly pH dependent as expected (*vide supra*), and the per cent conversion and product yields could be dramatically altered by changing the pH of the solution to be irradiated. The product yields shown in Fig. 2 are based on initial starting material and the per cent conversion is represented by the broken line. Mass balances were >90% except for experiments carried out at low pH values where additional unidentifiable HPLC peaks were observed.

Table 4 Concentration study[a]

Conc.[b]/ mol dm^{-3}	Irradiation[c] time/min	Conversion (%)	**1** (%)	**2** (%)	**3** (%)
0.05	4.0	10.2	47.0	13.1	33.6
0.01	1.0	13.2	43.4	14.2	35.4
0.001	0.1	15.2	44.5	13.3	35.0

[a] In methanol with 0.01 mol dm^{-3} Na_2HPO_4 as buffer. [b] Refers to concentration of metanilic acid. [c] Adjusted to achieve low percentage conversions.

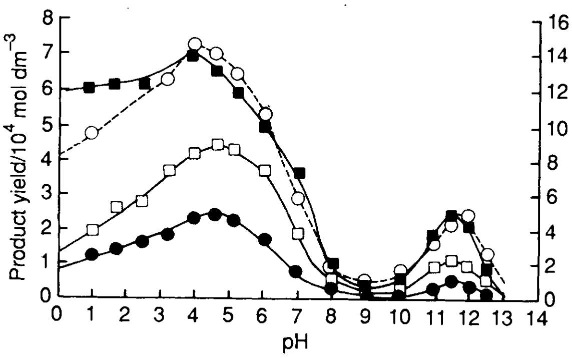


Fig. 2 pH Profile showing percentage conversion of metanilic acid (○) (right ordinate) after 1 min irradiation and the yield of aniline (■), orthanilic acid (●), and sulphanilic acid (□) (left ordinate), *versus* pH

There appear to be two distinct regions of catalysis; one between pH 10.5 and 12.5 and the other below pH 7.0. However, catalysis of the photoreaction is much more predominant at lower pH values. Furthermore, although there is a considerable fall-off in the isomerization yield, the yield of aniline decreases only slightly as the pH is lowered. The profile was not extended below pH 1.0 because of the possibility of competing thermal reactions of the products **2** and **3**.[3] In the pH range 7.5–10.5 no enhancement in product yield was observed although the acidity of the medium was changed by three orders of magnitude. This is interpreted as being due to the uncatalysed photoreaction, or more accurately to the reaction being catalysed by water.

Acid-base Catalysis of the Photoreaction.—Recent reports by Wubbels and Celander[11a] on a general-base catalysed photo-Smiles rearrangement and by Wan and Yates[11b] on general acid catalysis of the photohydration of aromatic alkenes prompted us to investigate the possibility of general acid or base catalysis of this photoisomerization. Aqueous solutions

Table 5 Sensitization[a]

Sensitizer	E_T[b]/ kcal mol^{-1}	Conc./ mol dm^{-3}	pH	Conversion (%)	Aniline (%)	Orthanilic acid (%)	Sulphanilic acid (%)
None[c]	—	—	4.2	19.2	37.8	15.6	38.4
			11.2	11.1	28.0	18.5	51.8
Benzene	84.3	0.2	4.2	24.6	36.1	17.2	38.2
			11.2	13.4	27.2	18.3	49.1
Acetophenone	73.7	0.1	4.2	—[d]	—[d]	—[d]	—[d]
			11.2	—[d]	—[d]	—[d]	—[d]

[a] Metanilic acid (0.01 mol dm^{-3}) in methanol with irradiation time of 1 min. [b] See ref. 50. [c] Refers to direct irradiation, *i.e.* without sensitizer. [d] Not detected.

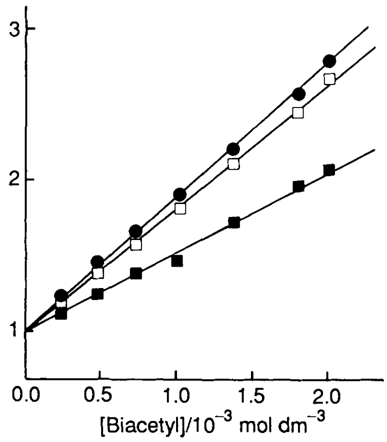


Fig. 3 Stern–Volmer plots for the appearance of orthanilic (●) and sulphanilic (□) acids and aniline (■). φ^0/φ is the ratio of the yield of product at zero quencher concentration to the yield of product at various quencher concentrations. $\varphi^0/\varphi = 1 + k_q\tau\,[Q]$.

of metanilic acid (0.01 mol dm^{-3}) at pH 5.2 and 6.1 containing varying amounts of NaH_2PO_4 were irradiated for 1 min in the Rayonet reactor. The results of these irradiations are presented in Tables 2 and 3. A general-acid catalysed isomerization process at these pH values is indicated by the increased yields of **2** and **3** with increasing buffer concentration. Such an observation constitutes the standard experimental test for general acid catalysis in the ground state.[12] Accordingly we conclude that these observations are indicative of the photoreactions being subject to general acid catalysis. However, we must remember that general acid catalysis is kinetically indistinguishable from general base–specific acid catalysis. The increase in isomerization yield is found to be linear up to 0.75 mol dm^{-3} buffer concentration after which the yield shows practically no dependence on buffer concentration. We feel that this pronounced curvature could be due to a change in the rate-determining step at high buffer concentrations. An example of this phenomenon can be found in general acid catalysed acetal hydrolysis.[13] Finally, the yield of aniline appears to be only slightly affected by increasing buffer concentration suggesting a specific acid catalysed process leading to its formation.

For practical reasons, buffer catalysis experiments can only be performed in the dilute acid region. We presume general acid catalysis can take place in the whole acidity region. Phosphate buffers were chosen because of their lack of UV absorption at wavelengths longer than λ = 220 nm, thus enabling photolyses to be carried out at λ = 254 nm. The use of acetic acid–sodium acetate as a buffer (pK_a = 4.75) proved to be unsuccessful since even 0.25 mol dm^{-3} solutions of the buffer absorbed significantly at λ = 254 nm (*A ca.* 0.30). On irradiation it was found that this absorption increased thus indicating that the buffer is photochemically labile. Finally, it was also noted that the photoreaction was subject to specific base catalysis at pH 11.6 because there was no change in product yields (within experimental error) with increasing buffer concentration. Na_3PO_4 was used as the general base at constant ionic strength.

Molecularity of the Isomerization.—The effect of varying the initial metanilic acid concentration on product distribution was examined at pH 4.5 in the presence of aqueous 0.01 mol dm^{-3} phosphate buffer. The results obtained from a fifty-fold variation in concentration are shown in Table 4. To achieve low percentage conversions the irradiation times had to be decreased as the substrate concentration was lowered. Within experimental error there was no change in product distribution on changing substrate concentration. This supports an intramolecular mechanism of isomerization. If the isomerization was intermolecular one would expect a fall-off in the yields of orthanilic and sulphanilic acids at low concentrations of metanilic acid.

Radical Scavenging.—In order to establish the presence or absence of radical intermediates in this photoreaction a methanolic solution of compound **1** (0.01 mol dm^{-3}) was irradiated for 1 min in the Rayonet reactor in the presence of the established radical scavenger n-butyl thiol (0.001 mol dm^{-3}). Comparing the results obtained from this experiment with those from the direct irradiation (Table 1) it was seen that there was no change in product yields or product distribution within experimental error after allowance was made for absorption by n-butyl thiol. Thus it appears that the photoreaction of compound **1** to give isomerization products and **4** proceeds through a non-radical process or mechanism.

Sensitization Experiments.—To investigate the possibility of a triplet pathway in the photoreaction of metanilic acid, triplet sensitization experiments employing acetophenone and benzene were carried out in methanol at pH 4.2 and 11.2 (Table 5). The concentration of the sensitizers was such that they absorbed >95% of the incident light in order to ensure selective excitation of the sensitizer. No triplet sensitized reaction could be observed with acetophenone (E_T = 73.7 kcal mol^{-1}).* However, the use of benzene (E_T = 84.3 kcal mol^{-1}) as sensitizer did prove effective in yielding the same photoproducts as those observed in the direct irradiation (*i.e.* without sensitizer). Furthermore, the sensitized irradiations at both pH values provide the same product distribution as obtained in the direct irradiation. The 'fingerprint' comparison[14] is suggestive of one triplet state, T_1, giving rise to the three photoproducts. This T_1 state can also be taken as having a triplet energy lying between 73.7 and 84.3 kcal mol^{-1}. In order to provide further insight into the multiplicity of the excited state quenching studies were carried out.

Quenching Studies.—Stern–Volmer (S–V) plots for the appearance of **2**–**4** on irradiation of metanilic acid in water

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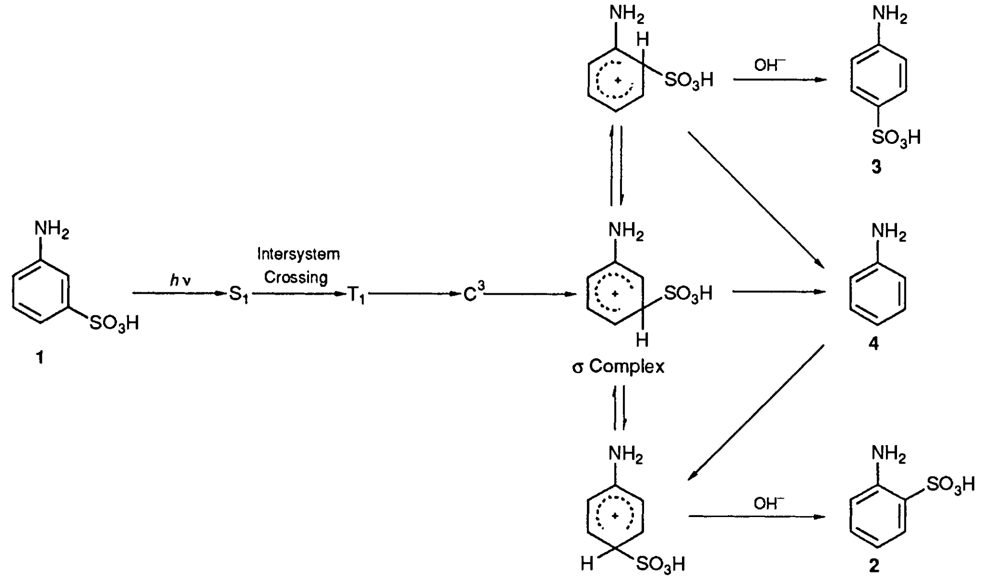
* 1 cal = 4.184 J.



Scheme 2

Table 6 Quenching data[a]

Compound	Slope ($k_q\tau$)/dm^3 mol^{-1}	Lifetime (τ)/10^{-7} s
Orthanilic acid	880	1.38
Sulphanilic acid	805	1.26
Aniline	515	0.805

[a] From S–V plots in Fig. 3.

with varying concentrations of the triplet quencher, biacetyl, were obtained (Fig. 3). The plots for the two anilinesulphonic acids were linear with similar slopes. Assuming the quenching to be diffusion controlled the value τ, the mean lifetime of an excited state of metanilic acid, may be estimated from the slopes, $k_q\tau$, of these two linear S–V plots. Hence, assuming the bimolecular diffusion controlled rate constant for neat water at 20 °C to be 6.4×10^9 dm^3 mol^{-1} s^{-1} on the basis of the Debye expression, the value τ was calculated for each slope (Table 6). Lifetimes of τ *ca.* 1.3×10^{-7} s for compounds **2** and **3** suggest that the isomerization proceeds through one excited triplet state, T_1.

Finally, additional evidence for triplet involvement in the photoreaction of metanilic acid was obtained from the effect of the known triplet quencher, oxygen, on the photolysis. When oxygen was bubbled through a methanolic solution of metanilic acid (0.01 mol dm^{-3}) before and during irradiation, no products were detected, in addition to there being negligible conversion of the substrate.

Mechanism of the Photoreaction of 1.—In view of the results obtained the mechanism presented in Scheme 2 is proposed for the photoisomerization and photodegradation of metanilic acid. The mechanism follows two separate pathways after protonation of metanilic acid in its triplet state. Initially, metanilic acid is excited to the first excited singlet state, S_1, after which intersystem crossing (ISC) to T_1 rapidly ensues. The configuration of the first excited singlet state, S_1, is undoubtedly $\Pi.\Pi^*$ in view of the large molar extinction coefficients for metanilic acid: λ^{H_2O}/nm 237 (3.2), 262 (2.5), 269 (2.6) and 289 (2.6).[15] It is not possible to give a state identification to T_1 with any degree of confidence, but rapid energy transfer from a Π,Π^* to an η,Π^* state is a distinct possibility. Interaction of a proton or hydroxonium ion with metanilic acid in its triplet state leads to the formation of an encounter complex or of an exciplex (C^3) which can either decompose into its components or convert into a σ-complex in the ground state where a number of possibilities exist. The σ-complex mechanism has previously been suggested to be involved in photochemical methoxide exchange in some nitromethoxybenzenes[16] and in the photo-Smiles rearrangement of β-(nitrophenoxy)ethylamines.[17]

The σ-complex may proceed to yield aniline which is essentially an electrophilic aromatic substitution process of the sulphonic acid group by hydrogen (H^+). Alternatively the σ-complex may, in the presence of base, revert to metanilic acid. These two processes involve separation of ionic species and thus an increase in solvent polarity will increase the possibility of an ionizing mechanism. Thus we get a high yield of aniline and a lower percentage conversion in water than in methanol. Finally the *meta* σ-complex may isomerize to the more stable *ortho* and *para* σ-complexes involving an intramolecular 1,2-shift of the sulphonic acid group. These two σ-complexes may then in the presence of base proceed to yield orthanilic and sulphanilic acids.

Since neither solvent or pH has an effect on the *ortho*/*para* ratio it is very unlikely that the sulphonic acid group becomes detached from the benzene ring and thus the isomerization is likely to involve a very tightly bound intermediate. Isomerization of σ-complexes has been the subject of much discussion by Shine[18] and has also been used to account for the isomerization of orthanilic to sulphanilic acid in concentrated sulphuric acid.[19]

It now remains to assign the rate-determining step(s) to this complex mechanism. The isomerization is subject to either general acid or general base–specific acid catalysis at acidic pH values. The former implies that metanilic acid is converted into the σ-complex in a slow rate-determining step followed by a relatively fast step which does not involve base, giving rise to isomerization products. Alternatively, general base-specific acid catalysis involves a fast protonation step giving rise to the σ-complex followed by a rate-determining step which involves attack by a base. We feel that the latter form of catalysis is operative in our case as it accounts for the specific-acid catalysis of aniline formation *i.e.* a fast protonation step followed by a rate-determining step which does not involve base. In the formation of orthanilic and sulphanilic acid we have a rate-determining proton abstraction by the base from the *ortho* and *para* σ-complexes.

However, at pH 11.3 we have found the photoreaction to be subject to specific base catalysis which essentially means that we have rapid proton abstraction from the σ-complex and thus protonation of metanilic acid becomes rate-determining. Therefore the curvature observed in the buffer catalysis experiments at pH 5.2 and 6.1 when the data in Tables 2 and 3 are plotted can be attributed to a change in the rate-determining step as initially suspected. The small degree of base catalysis relative to acid catalysis observed (Fig. 2) is probably due to the small concentrations of hydrogen ion, water or hydroxonium ion present at alkaline pH values. The depletion of water on going to strongly acidic or alkali solutions would reasonably account for the fall-off in percentage conversion at low and high pH values. Finally, the relative insensitivity of aniline formation to acidic pH is due to its mechanism of formation. The rate-determining step of loss of the sulphonic acid group does not require the presence of base which would be present in very low concentration at low pH values. To conclude the mechanistic interpretation, we feel that the strongest evidence for the mechanism shown is its capacity to account for the above-mentioned anomalies.

To the best of our knowledge this photoreaction is only the third reported example of a general-catalysed process. The first was reported by Wubbels and Celander[11a] for the general-base catalysed photo-Smiles rearrangement of β-aminoalkylnitrophenylethers in water which was followed shortly afterwards by a report by Wan and Yates[11b] on the general-acid catalysed photohydration of a number of substituted aromatic alkenes and alkynes. The photoreaction appears to be another example of a truly catalysed photochemical process according to Wubbels' definition since the 'photocatalysis' is due to an increased efficiency of reaction of an excited state. The photoisomerization of metanilic acid is an example of the '*meta*' effect or reversal of ground state reactivity[20] in that the other two isomers orthanilic and sulphanilic acid do not photoisomerize which is opposite to the ground state behaviour where metanilic is the only isomer not to undergo isomerization. Finally, we have computed charge distributions for the ground and lowest triplet states of the anilinesulphonic acids to see if there is a correlation between the observed reactivities of the sulphonic acids and the computed charge densities at the carbon atoms.[21] No correlation was found but the theoretical calculations do show that the 2-, 3- and 4-carbons both in the ground and lowest triplet states for orthanilic, metanilic and sulphanilic acids, respectively, are the positions most likely to protonate and accordingly in Scheme 2 the protonation is shown at these positions.

Experimental

Materials and Methods.—All solvents were either HPLC or Analar grade and were used without further purification. Acetic acid, orthophosphoric acid, sodium dihydrogen orthophosphate, disodium hydrogen orthophosphate, trisodium phosphate and sodium acetate were Analar grade. All other reagents were commercially available and were used as obtained. pH adjustments were made with either dilute H_3PO_4 or NaOH except in the case of the buffer catalysis experiments where dilute perchloric acid was used. Benzene, acetophenone and biacetyl were distilled before use. The sodium salts of the isomeric anilinesulphonic acids, which were used in all runs because of their greater solubility, were prepared by treating a suspension of the acid (3 g) in 50 cm^3 of methanol–water, 50/50 (v/v) with 20% NaOH until it became alkaline. The resulting solution was evaporated to dryness under reduced pressure and recrystallized several times from methanol–water, 95/5 (v/v). The buffer catalysis experiments were carried out at constant ionic strength (1.0 mol dm^{-3}). In all irradiations the pH was checked before and after photolysis. A Pye-Unicam Model 290MK2 pH meter standardized with buffers of pH 4.0, 7.0 and 9.2 was used for pH measurements. UV spectra were recorded at room temperature using a Shimadzu UV-260 spectrophotometer. HPLC analyses were performed using an Applied Chromatography Systems LC 750 model.[22] The irradiation apparatus and procedure was as described previously.[23] UV monitoring, concentration studies, radical scavenging, sensitization and quenching experiments were carried out as described previously.[23] The sulphate anion was detected in irradiated methanolic and aqueous solutions of metanilic acid.[24] No thermal reaction was detected by any pH.

HPLC Analysis.—The products separated by HPLC were identified by comparison of retention times with those of authentic samples. External standard calibration curves were used for assaying the mixture of products of photolyses. The pH of the solutions at low and high pH values was adjusted to a neutral value before analysis by HPLC. A Spherisorb 10 mm^3 ODS column (HPLC Technology) was used for all HPLC analysis. For analysis of the reaction mixture obtained from the irradiation of either of the anilinesulphonic acids the mobile phase consisted of a 15% acetonitrile–water mixture containing 0.05 mol dm^{-3} Na_2HPO_4 and 0.005 mol dm^{-3} tetrabutylammonium hydrogen sulphate (TBAHS) adjusted to pH 6.5. The flow rate was 2 cm^3 min^{-1} and detection (UV) was at $\lambda =$ 254 nm. The retention times for sulphanilic acid, metanilic acid, orthanilic acid and aniline were 2.2, 2.8, 4.5 and 5.9 respectively.

MO Calculations.—Molecular orbital calculations were carried out using the Quantum Chemistry Programme Exchange (QCPE) number 506 (AMPAC)[25] which is a variation of MNDO. The basis for the calculations were the previously published crystal structures of orthanilic,[26] metanilic[27] and sulphanilic[28] acids. The calculations were carried out for the anion of the acid as this is the species which would be present at pH values greater than 4.0 in view of the pK_a values for orthanilic, metanilic and sulphanilic acids (2.46, 3.74 and 3.23, respectively).[29] Ground state calculations were carried out with full geometry optimization and the excited state calculations were carried out at the optimized ground state geometry. There was very good agreement with the calculated excitation energies and those experimentally observed for metanilic and sulphanilic acids. However, the agreement for orthanilic acid was very poor which probably indicates that the assumption of the same geometry in both ground and excited states is incorrect for orthanilic acid.

Acknowledgements

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References

1 E. Bamberger and J. Kunz, *Ber.*, 1897, **30**, 2274.
2 W. J. Spillane and F. L. Scott, *Tetrahedron*, 1968, **24**, 5011.
3 R. N. Khelevin, *Zh. Org. Khim.*, 1981, **17**, 1849; 1984, **20**, 791; R. N. Khelevin, *Zh. Obshch. Khim.*, 1984, **54**, 747; R. N. Khelevin, *Zh. Org. Khim.*, 1990, **26**, 155.
4 Y. Ogata, K. Takagi and S. Yamada, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2205.
5 Y. Izawa, N. Suzuki, A. Inoue, K. Ito and T. Ito, *J. Org. Chem.*, 1979, **44**, 4581 and references cited therein.
6 M. Kimura and Y. Ogata, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 471.
7 N. Suzuki, K. Ito and Y. Izawa, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 1591.
8 Y. Ogata, K. Tagaki and S. Yamada, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1629.
9 Y. Izawa and N. Kuromiya, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3197.
10 J. P. Pete and C. Portella, *Bull. Soc. Chim. Fr.*, 1980, **2**, 280.

11 (*a*) G. G. Wubbels and D. W. Celander, *J. Am. Chem. Soc.*, 1981, **103**, 7669 and see *J. Am. Chem. Soc.*, 1982, **104**, 2677 for correction; (*b*) P. Wan and K. Yates, *J. Org. Chem.*, 1983, **48**, 869.

12 W. P. Jencks, *Catalysis in Chemistry and Enzymology*, McGraw–Hill, New York, 1969, ch. 3.

13 T. H. Fife and R. Natarajan, *J. Am. Chem. Soc.*, 1986, **108**, 8050.

14 H. E. Zimmermann and J. W. Wilson, *J. Am. Chem. Soc.*, 1968, **90**, 3749.

15 Handbook of Chemistry and Physics, 60th edn., CRC Press Inc., 1980, p. C-176.

16 H. C. H. A. van Riel, G. Lodder and E. Havinga, *J. Am. Chem. Soc.*, 1981, **103**, 7257.

17 G. G. Wubbels, A. M. Halverson, J. D. Oxman and V. H. De Bruyn, *J. Org. Chem.*, 1985, **50**, 4499.

18 H. J. Shine, *Aromatic Rearrangements*, Elsevier, 1967, p. 2.

19 F. L. Scott and W. J. Spillane, *J. Chem. Soc. B*, 1968, 779.

20 E. Havinga, R. O. De Jongh and W. Dorst, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 378; E. Havinga, *Verslag Kon Ned. Ak. Wet Afd. Natuurk*, 1961, **70**, 52; H. E. Zimmermann and V. R. Sandel, *J. Am. Chem. Soc.*, 1963, **85**, 915; H. E. Zimmermann and S. Somasekara, *J. Am. Chem. Soc.*, 1963, **85**, 922.

21 Using QCPE programme 506 (AMPAC).

22 W. J. Spillane, J. M. Lally, K. McCormack and F. Kanetani, *Analyst*, 1988, **113**, 399.

23 J. M. Lally and W. J. Spillane, *J. Chem. Soc., Perkin Trans. 2*, in the press (paper 0/03437A).

24 F. Feigl, *Spot Tests in Inorganic Analysis*, Elsevier, 5th edn., 1958, pp. 307 and 314.

25 James J. P. Stewart, Dewar Group, University of Texas, Austin, Texas 78712, USA.

26 S. R. Hall and E. N. Maslen, *Acta Crystallogr.*, 1967, **22**, 216.

27 S. R. Hall and E. N. Maslen, *Acta Crystallogr.*, 1967, **18**, 301.

28 I. A. I. M. Rae and E. N. Maslen, *Acta Crystallogr.*, 1962, **15**, 1285.

29 Ref. 15. Handbook of Chemistry and Physics, 60th edn., CRC Press Inc., 1980, p. D–165.

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