The Photochemistry of Metanilic Acid : Photoisomerization and Photodegradation

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In the photolysis of sodium metanilate (1,Na) a single triplet and a series of σ-complexes give rise to the isomeric aniline sulphonic acids (2) and (3) and aniline (4).
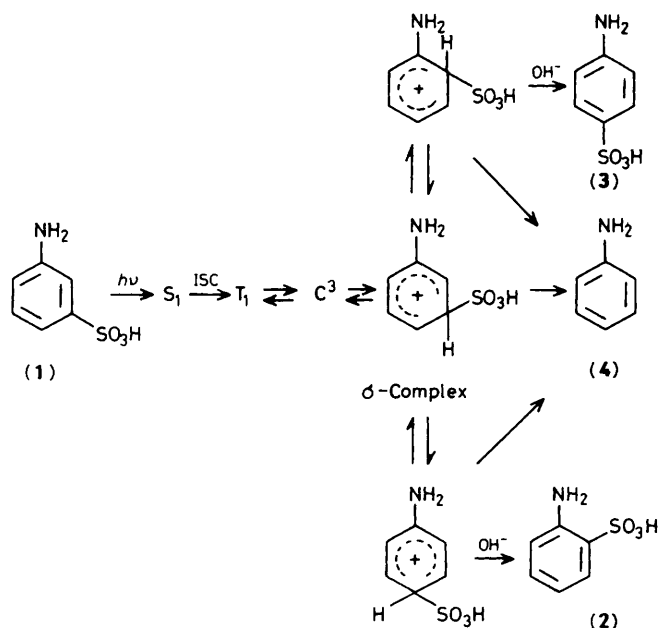
The thermal isomerization of orthanilic (2) and sulphanilic (3) acids in concentrated sulphuric acid at high temperatures is well known[1—5] and has been studied extensively by Khele-vin.[3—5] Metanilic acid does not isomerize under similar conditions. Following our study of the photochemistry of phenylsulphamic acid[6] we now report the first photochemical isomerization of the sodium salt of metanilic acid (1,Na) to give the ring-substituted sulphonic acids (2) and (3) and the photodegradation product, aniline (4). When metanilic acid was irradiated in water at low % conversion through quartz under helium at 254 nm the products (2)—(4) were formed. Compounds (2) and (3) did not undergo photoisomerization under similar conditions. This report provides a further example[7] of a photoisomerization of a ring-substituted aromatic and it is also an additional example of the 'meta' effect or reversal of ground state reactivity in the excited state.[8]

The photoreaction was found to be strongly pH and solvent dependent. The pH profile (Figure 1) shows the photoreaction to be subject to both acid and base catalysis, the former being much more predominant. The fall-off in product yields at low and high pH may be attributed to the depletion of water on going to strongly alkali or acidic media.† However as the pH is lowered, there is only a slight decrease in the yield of (4). The use of methanol as solvent results in higher % conversions and higher yields of isomerization products (2) and (3) (Table 1). The apparent insensitivity of the *ortho/para* ratio to variation in pH and solvent suggests the involvement of a tightly bound

intermediate leading to the formation of (2) and (3). In all cases the mass balance was >90% indicating a relatively clean reaction.

Buffer catalysis experiments indicate that the photoisomer-ization is a general-acid-catalysed process of which there is only one previous report.[9] There was a linear increase in the yields of (2) and (3) with increasing concentration of buffer (NaH_2PO_4–Na_2HPO_4) at pH 5.2 and 6.1. However there was no change in the yield of aniline, thus indicating a specific-acid-catalysed process leading to its formation. It was found that the radical scavenger n-butyl thiol did not have any effect on the photoreaction indicating a non-radical mechanism. Finally, sensitization and quenching experiments provided evidence for the participation of the first excited triplet state (T_1) in the photoreaction. Sensitization with benzene (0.1M) in methanol yielded the same product distribution as that observed in the direct irradiation ('fingerprint' comparison[10]) and the photoreaction was efficiently quenched by biacetyl and oxygen.

The mechanism shown in Scheme 1 is proposed for the photoreaction. Rapid protonation of metanilic acid‡ in its triplet state may lead to the formation of an encounter complex or an exciplex (C^3) which can either decompose into its components or be converted into a σ-complex in the ground state, where a number of possibilities exist. The σ-complex mechanism has previously been suggested as being involved in photochemical methoxide exchange in some nitromethoxy-benzenes[11] and in the photo-Smiles rearrangement of β-(nitrophenoxy)ethylamines.[12] The σ-complex may proceed to yield (4) in a process which is essentially an electrophilic aromatic replacement of the sulphonic acid group by a proton. The intermediacy of σ-complexes in such processes is well established.[13] Dissociation of the σ-complex to give aniline is a slow step which does not involve base. Hence the yield of (4) is relatively insensitive to low pH values. Alternatively the σ-complex may, in the presence of base, revert to (1). These two processes involve separation of ionic species and thus an

Scheme 1

Figure 1. pH Profile showing % conversion (○) (right ordinate) and the yields of aniline (■), orthanilic acid (●), and sulphanilic acid (◆) (left ordinate) *vs.* pH.

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† Products were determined by reversed-phase h.p.l.c. using external standard calibration curves. The pH of the solutions at low and high pH values was adjusted to 7 before analysis.
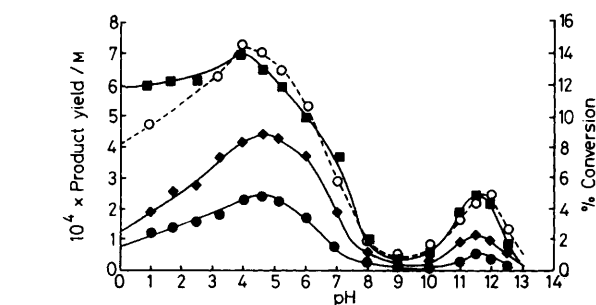
‡ M.O. calculations (see text) indicate that protonation will take place at the C.

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

pH	Solvent	Conversion, %	Aniline, %	Orthanilic acid, %	Sulphanilic acid, %	o/p	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] 0.01M in metanilic acid and 1 min irradiation time. [b] % Yields based on consumed starting material. [c] Refers to ratio of yield of degradation product, aniline (4), to yield of isomerization products, (2) + (3).

increase in solvent polarity will increase the possibility of an ionizing mechanism, leading to a higher yield of (4) and a lower % conversion in water than in methanol. Finally the *meta* σ-complex may isomerize to the more stable *ortho* and *para* σ-complexes *via* a 1,2-shift of the sulphonic acid group. These complexes may, in a slow step, then either yield (4) as before or in the presence of base yield (2) and (3).

The predominance of *meta* regioselectivity may be explained by the 'energy gap' model previously proposed to explain the predominance of *meta* substitution in photochemical methoxide exchange in some nitromethoxybenzenes[11] and later used to account for the reversal of reactivities observed in a study on the regioselectivity of photochemical and thermal Smiles rearrangements.[12] The regioselectivity of (1) is rationalized on the basis of the smaller energy gap between the ground state σ-complex and the excited state encounter complex (C³) compared to those for (2) and (3).

Theoretical calculations[14] showed that there was no correlation between the observed reactivities of (1), (2), and (3) and the charge densities at the carbon atoms bonded to the sulphonic acid group.

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