The Photochemistry of Phenylsulphamic Acid: Photorearrangement and Photodegradation

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Photolysis of the sodium salt of phenylsulphamic acid (**1, Na**) yields the isomeric aniline sulphonic acids (**2**)—(**4**) and aniline (**5**); the involvement of an intramolecular radical rearrangement and two triplet states in the photoreaction are supported.

The thermal rearrangement of phenylsulphamic acid (**1**) has been known since 1897[1] and has been the subject of considerable attention since then.[2] We now report the first photochemical rearrangement of the sodium salt (**1, Na**) to give the ring-substituted sulphonic acids (**2**)—(**4**) and the photodegradation product, aniline (**5**). When compound (**1, Na**) was irradiated at low percentage conversions (<12%) through quartz under helium in various solvents at 254 nm the products (**2**)—(**5**) were formed [*e.g.* in MeOH, (**2**) 22.0%, (**3**) 5.1%, (**4**) 39.4%, and (**5**) 27.0% yields].† This new photoarrangement is analogous to the photo-Fries type rearrangement of which numerous examples are known,[3] and where the generally accepted mechanism is that of a radical cage, originating from the first excited singlet state, giving rise to both rearrangement and degradation products. The *meta*-oriented product has been detected in only a few cases in these *ortho–para* photo-Fries type rearrangements.[4]

The involvement of an intramolecular radical rearrangement in the photolysis of (**1, Na**) is supported by the absence of a concentration effect over a fifty-fold variation in substrate concentration (0.001 M—0.005 M) and by a considerable lowering in the yields of (**2**)—(**4**) when the irradiation is carried out in the presence of the radical scavenger, n-butyl thiol. Sensitization with benzene and anisole (both 0.1 M in MeOH) yielded the same photoproducts as those obtained in the unsensitized irradiation, indicating triplet state participation in the photoreaction, although the differing product distributions obtained in the unsensitized and sensitized runs suggest the possible participation of more than one excited state.

In order to provide further information on the multiplicity of the excited state(s) involved, Stern–Volmer plots for product formation in methanol were constructed using *trans*-penta-1,3-diene as quencher (Figure 1). Lifetimes of $\tau \sim 2 \times 10^{-7}$ s for (**2**)—(**4**) suggest that the rearrangement proceeds through one excited triplet state (T_1). However, the curved nature of the aniline plot reflects the involvement of two discrete excited states leading to its formation. The state

Table 1. Relative T_1/T_2 contributions to aniline formation.

Solvent	Aniline/%	Intercept	Aniline(T_1)/ %	Aniline(T_2)/ %
Methanol	28.0	1.48	9.1	18.9
Ethanol	37.5	2.90	24.6	12.9

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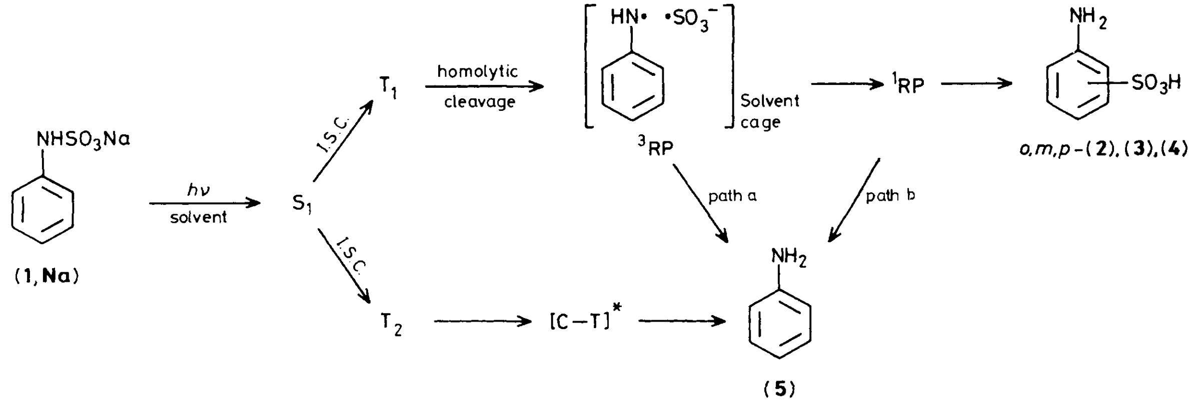
† % Yields are based on consumed (**1, Na**) and were determined by reversed-phase h.p.l.c. 0.01 M solutions of (**1, Na**) were irradiated for 1 min in a Rayonet photochemical reactor (254 nm). The sulphite anion was also detected. The photostabilities of the compounds (**2**)—(**4**) were checked over the period of the rearrangement.



Scheme 1

arising from the steep slope corresponds to a lifetime of 2.13 × 10^{-7} s while that arising from the shallower slope corresponds to a lifetime of 5.1 ± 1.1 × 10^{-9} s.‡ The similarity of the former value to that obtained for the T_1 state suggests that aniline also arises from the triplet rearrangement state and from a short-lived state which could be a singlet or a short-lived triplet state. However, a linear Stern–Volmer plot for fluorescence quenching gave an excited singlet state lifetime of 9.4 ± 5.2 × 10^{-10} s, and thus aniline arises from two triplet states (T_1 and T_2). The relative contribution to aniline formation from each of these states can be calculated from the intercept in the Stern–Volmer plots for aniline formation in both methanol and ethanol (Table 1).

On the basis of the above results the mechanism presented in Scheme 1 is proposed for the photoreaction.§ Reaction from T_1 involves homolytic cleavage of the nitrogen–sulphur σ-bond to give a triplet radical pair (^{3}RP), which must first, through hyperfine coupling, undergo intersystem crossing (I.S.C.) to a singlet pair (^{1}RP) before undergoing cage coupling reactions to give the rearranged products (**2**)—(**4**). Hence the relatively long lifetime of the ^{3}RP allows a competition to be set up between I.S.C. within the solvent cage and escape of the radical pair from the cage. Then the anilino radical reacts with the solvent yielding aniline (path a). Alternatively aniline may be formed from the ^{1}RP (path b), although this route is unlikely to be a very important one in view of the efficiency of recombination for a ^{1}RP. Enhanced reaction from T_2 by the more polar solvent, methanol, could be due to the intermediacy of a charge transfer complex [C-T]* although we have no direct evidence for this.

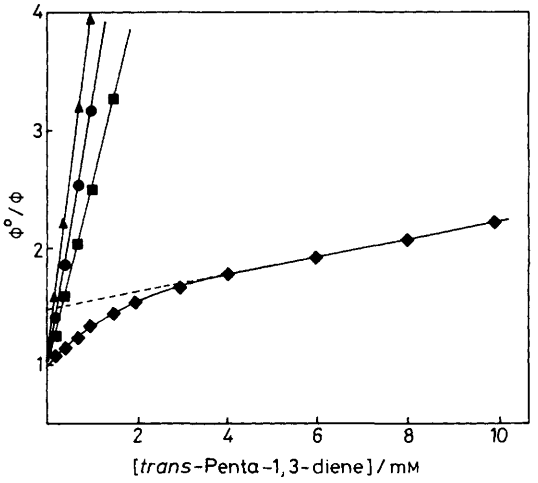


Figure 1. Stern–Volmer plots for the appearance of *ortho-* (●), *meta-* (▲), and *para-* (■) aniline sulphonic acids, and aniline (◆). ϕ^0/ϕ is the ratio of the yield of product at zero quencher concentration to the yield of product at various quencher concentrations.

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‡ The lifetime of the long-lived state was derived by subtracting the extrapolated ϕ^0/ϕ values from the experimental ones and plotting the reciprocal of this difference against diene concentration. That for the short-lived one was derived from the ratio of slope to intercept of the linear portion of the plot. The two corresponding plots are linear with slopes $k_q\tau$. The lifetime of the short-lived state is the average of three determinations. A similar curved Stern–Volmer plot was also obtained using biacetyl as quencher.

§ (a) Our data do not permit us to decide the origin of the two triplet states, *i.e.*, whether T_1 and T_2 arise from the first excited singlet state S_1 only, or from the first and second excited singlet states, or whether T_1 arises only from T_2 through rapid internal conversion, or any other combination of the above. Thus the route shown for T_1 and T_2 generation is only one of several possibilities.

(b) The configuration of the first excited singlet states is undoubtedly π,π* in view of the large molar extinction coefficients for (**1, Na**); λ (MeOH) 233 (11 000) and 278 (1200) nm. However, we are unable to give state identifications to T_1 and T_2 with any degree of confidence, rapid energy transfer from π,π* to n,π* states being a distinct possibility, especially since the sulphonate group introduces the low-lying ^{1,3}(n, π)* states. Such energy transfer has recently been the subject of mechanistic studies by Zimmerman *et al.*[5] with bichromophoric molecules.