The Wallach Rearrangement in 100% Sulphuric Acid

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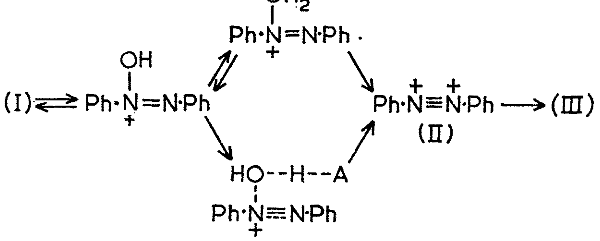
KINETIC study of the Wallach rearrangement[1] of azoxybenzene (I) in moderately concentrated sulphuric acid solutions[2] implicated the involvement of a two-proton process, which was interpreted in terms of a dicationic intermediate (II),[3] formed by two alternative routes, reacting with solvent water to give the 4-hydroxyazobenzene product (III). Alternative mechanisms have been suggested by other workers.[4] It seemed worthwhile to extend the study to the 100% H_2SO_4 region, in which medium stabilization of the suggested dicationic intermediate appeared to be a possibility.

As an initial approach, the cryoscopic and conductivity behaviour of azoxybenzene in 100·0% H_2SO_4 was examined.



This gave a cryoscopic ν value[5] of 3·8, increasing over a period of days to 4·8, and a conductivity γ value[5] of 2·0, increasing to 2·5. Formation of intermediate (II) by the above scheme requires $\nu = 5$, $\gamma = 3$ according to the equation

$$(I) + 3H_2SO_4 \rightarrow (II) + H_3O^+ + 3HSO_4^-.$$

Diprotonation of the reactant would lead to $\nu = 3$, $\gamma = 2$. A combination of the two processes could possibly account for the experimental data.

Spectral examination of azoxybenzene in 100·0% H_2SO_4 at 25° some minutes after mixing showed the presence of a new absorption at 426 nm. (ϵ 3·26 × 10^4), which increased slightly and simultaneously shifted to 430 nm. over 1 hr. The monoprotonated forms of azoxybenzene and 4-hydroxyazobenzene have absorptions in 80—95% H_2SO_4 at 390 and 460 nm., respectively. Azobenzene, which has some structural analogy to (II), has absorption in 100% H_2SO_4 at 424 nm. Unexpectedly, the spectrum of 4-hydroxyazobenzene in 100·0% H_2SO_4, taken a few minutes after preparation, appeared identical in all respects with that given by azoxybenzene and showed the same time variation.

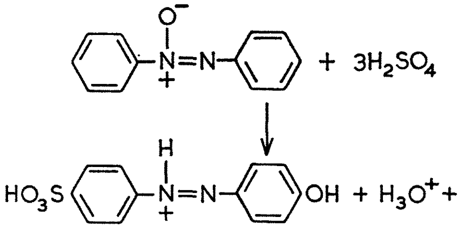
A systematic study undertaken with 4-hydroxyazobenzene as substrate showed a rather complex pattern of spectral changes, resulting from both equilibrium and rate processes not defined hitherto. Between 96 and 100% H_2SO_4 the 460 nm. absorption due to protonated 4-hydroxyazobenzene undergoes lateral shift to 426 nm., which is assigned to a second equilibrium protonation [pK^2_a — 10·2, λ_{max} (BH_2^{2+}) 426 nm.]. Thus in 100·0 + % H_2SO_4 (H_0 —11·1)[6] 4-hydroxyazobenzene is almost 90% diprotonated. Above 90% H_2SO_4, spectra of 4-hydroxyazobenzene show in addition a time-dependency, which is identified as the result of sulphonation, to give 4-hydroxyazobenzene-4′-sulphonic acid [λ_{max} (BH^+) 465 nm.][7] The pseudo-first-order constant of this reaction at 25° increases from 5·1 × 10^{-6} sec.$^{-1}$ in 91·66% H_2SO_4 to 2·50 × 10^{-3} sec.$^{-1}$ in 99·94% H_2SO_4, beyond which the rate levels off. 4-Hydroxyazobenzene-4′-sulphonic acid also undergoes a second equilibrium protonation [pK^2_a — 11·1, λ_{max} (BH_2^{2+}) 420 nm.], so that, depending on the acid concentration, the final absorption in the reaction of 4-hydroxyazobenzene to the 4′-sulphonic acid is observed between 465 and 420 nm.

In sulphuric acid solutions $\geqslant$100%, 4-hydroxyazobenzene exhibits a further, much slower, spectral process which is characteristic of a second sulphonation. In 100·07% the rate constant for the second sulphonation process at 25° is 1·2 × 10^{-5} sec.$^{-1}$. The second sulphonation product, probably 4-hydroxyazobenzene-3,4′-disulphonic acid, absorbs at 449 nm. (ϵ 4·45 × 10^4) in this medium. A kinetic run with 4-hydroxyazobenzene-4′-sulphonic acid as reactant in 100·07% H_2SO_4 duplicates precisely the spectral changes corresponding to the *second* sulphonation of 4-hydroxyazobenzene and shows no other features.

The kinetics of the Wallach rearrangement of azoxybenzene have been extended from 96 to 100% H_2SO_4 at 25°. An isosbestic point is observable until *ca.* 98% H_2SO_4, corresponding to formation of 4-hydroxyazobenzene (followed at 460—463 nm., as previously).[2] Above 99% H_2SO_4, where sulphonation of 4-hydroxyazobenzene becomes competitive, the rearrangement process was followed at the wavelength (422—430 nm.) corresponding to the isosbestic point of the consecutive reaction, the conversion of 4-hydroxyazobenzene into the 4′-sulphonic acid. The rate of rearrangement increased steadily from 2·8 × 10^{-4} sec.$^{-1}$ in 96·3% H_2SO_4 to 4·10 × 10^{-2} sec.$^{-1}$ in 99·99% H_2SO_4, the upper limit of this kinetic method. A kinetic run performed with azoxybenzene in 100·07% H_2SO_4 showed features identical in all respects to those observed with 4-hydroxyazobenzene, affording only rate constants for sulphonation of the initial rearrangement product.

These results show that the behaviour of azoxybenzene in 100·0% H_2SO_4 is accountable in terms of a rapid rearrangement to 4-hydroxyazobenzene ($t_{\frac{1}{2}}$ < 0·5 min.) followed by two consecutive sulphonation reactions ($t_{\frac{1}{2}}$ 4·5 min. and 28 hr., respectively). No compelling evidence was found to indicate the existence of reaction intermediates, (II)[3] or others,[4] *in finite concentration* but diprotonation of 4-hydroxyazobene and of 4-hydroxyazobenzene-4′-sulphonic acid results in the appearance of new absorbing species in 100% H_2SO_4.

The cryoscopic and conductivity data obtained for azoxybenzene in 100·0% H_2SO_4 can now be ascribed to the essentially complete conversion of azoxybenzene into 4-hydroxyazobenzene-4′-sulphonic acid by the time the first measurements can be taken.† The subsequent slow increase in ν, γ is due to partial conversion into the disulphonic acid. As required by the overall scheme, 4-hydroxyazobenzene gave cryoscopic and conductivity data equal, within experimental error, to those obtained with azoxybenzene as substrate.



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† The kinetic and equilibrium data obtained spectrally for azoxybenzene in 100·0% H_2SO_4 cannot be correlated directly with the cryoscopic and conductivity results, due to the different substrate concentrations used (1 × 10^{-5}—5 × 10^{-5}M for the former, 2 × 10^{-2}—4 × 10^{-2}m for the latter) as well as the lower temperature (10°) used in cryoscopy. The sulphonation reaction causes (as a result of the liberation of H_2O) a significant dilution of the medium, which will decrease the extent of diprotonation of the monosulphonic acid as well as the rate of sulphonation.

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