Interaction of Aniline with Diazotising and Nitrating Agents in Concentrated Sulfuric Acid

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The interaction of aniline with nitrosonium hydrogensulfate then with nitric acid in concentrated sulfuric acid does not occur through diazotisation and subsequent nitration of the benzenediazonium ion, but instead involves nitrosonium ion catalysed nitration of anilinium ion in the *para*-position together with uncatalysed nitration in the *meta*- and *para*-positions followed by diazotisation on dilution with water.

The diazonium group is the strongest electron-withdrawing substituent (σ_p 1.9–2.1).[1] However, information about its effect on the reactivity of the aromatic ring in electrophilic substitutions are contradictory. It was reported that the benzenediazonium ion is not nitrated in concentrated sulfuric acid,[2] is nitrated with difficulty in the *meta*-position[1] and is readily nitrated mostly in the *para*-position after diazotisation of amine in sulfuric or hydrofluoric acid.[3] Abnormal *para*-orientation was explained[4] by the influence of a diazo compound stabilizer such as anthraquinone-2,7-disulfonic acid. The present work has been undertaken to clarify this question.

It was established that the consequent treatment of aniline in 92% sulfuric acid with nitrosonium hydrogensulfate and nitric acid followed by dilution with water and azo coupling with *N*,*N*-diethylaniline leads to a mixture of *p*- and *m*-nitro azo compounds, while the *p*-nitro isomer predominates both in the presence and in the absence of a diazonium ion stabilizer, which is therefore of no importance. When the concentration of sulfuric acid is increased from 92% to 95% and 100%, the *para*/*meta* ratio of nitro isomers is decreased from *ca.* 3:1 to *ca.* 1.5:1 and *ca.* 1:1, respectively (Table 1). When the acidity is decreased below 85% sulfuric acid, a mixture of *p*-nitro and unnitrated azo compounds is formed.

^{1}H and ^{13}C NMR investigations show that anilinium ions in 92–100% sulfuric acid are practically unchanged in the presence of nitrosonium hydrogensulfate. Addition of nitric acid to a solution containing anilinium and nitrosonium ions causes the appearance of *p*- and *m*-nitroanilinium ions.[†] The treatment of a previously prepared benzenediazonium salt with nitric acid gives only azo compound without the nitro group, in accordance with ref. 2.

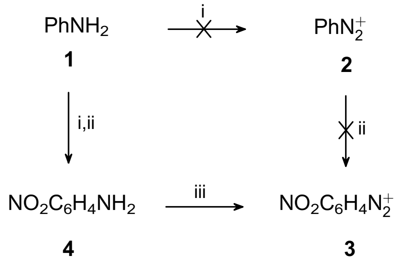
Table 1 Ratio of nitro isomers in the reaction of anilinium ion with nitric acid in concentrated sulfuric acid in the presence and in the absence of nitrosonium hydrogensulfate.

H_2SO_4 concentration (%)	Molar ratio $NO^+HSO_4^-/PhNH_2$	Ratio of *para*/*meta* isomers
92.5	1:1	74:26
92.4	–[a]	47:53
92.5	2:1	80:20
92.5	0.2:1	65:35
95.5	1:1	59:41
95.4	–[a]	43:57
100	1:1	49:51
100	–[a]	36:64

[a] In the absence of $NO^+HSO_4^-$, ref. 5.

Formation of nitrobenzenediazonium salts **3** from aniline under action of nitrosonium hydrogensulfate and then of nitric acid in concentrated sulfuric acid with subsequent pouring into water was interpreted[3,4] as diazotisation of aniline **1** and nitration of benzenediazonium ion **2**. Our results testify to nitration of aniline **1**, as anilinium ion, in the presence of nitrosonium ion to form nitroanilines **4**, which are diazotised after dilution with water to give nitrobenzenediazonium salts **3**. Anilinium ion is not diazotised and benzenediazonium ion is not nitrated in concentrated sulfuric acid.

The presence of nitrosonium ion on nitration of anilinium ion increases the proportion of *para*-substitution. That is evident on comparison with data for the reaction in the absence of nitrosonium hydrogensulfate at the same acidity[5] (Table 1).[‡] For example, the *para*/*meta* ratio is 47:53 in 92% sulfuric acid in the absence of nitrosonium hydrogensulfate and 74:26 in the presence of 1 mol of it. The nitrosonium ion effect is also illustrated by the dependence of the nitro isomer ratio on the relative quantities of nitrosonium hydrogensulfate. When the initial molar ratio of nitrosonium hydrogensulfate and aniline is changed from 1 to 2 and 0.2 the *para*/*meta* ratio is increased from *ca.* 3:1 to 4:1 and decreased to *ca.* 2:1, respectively (Table 1).



Scheme 1 *Reagents and conditions*: i, $NO^+HSO_4^-$, H_2SO_4; ii, HNO_3, H_2SO_4, room temp.; iii, H_2O.

The inability of aniline to be diazotised in concentrated sulfuric acid may be explained by Ridd's mechanism of diazotisation in highly acid media.[6,7] The mechanism involves the interaction of NO^+ with aromatic π-electrons of anilinium ion **5**, transformation of dicationic π-complex **6** (perhaps in two steps)[8] by deprotonation and migration of NO^+ in complex **7** to form *N*-nitrosammonium ion **8**, followed by a slow rate-determining step of proton transfer from the nitrogen of cation **8** to the solvent and a series of fast steps leading to diazonium ion. As acidity is increased the

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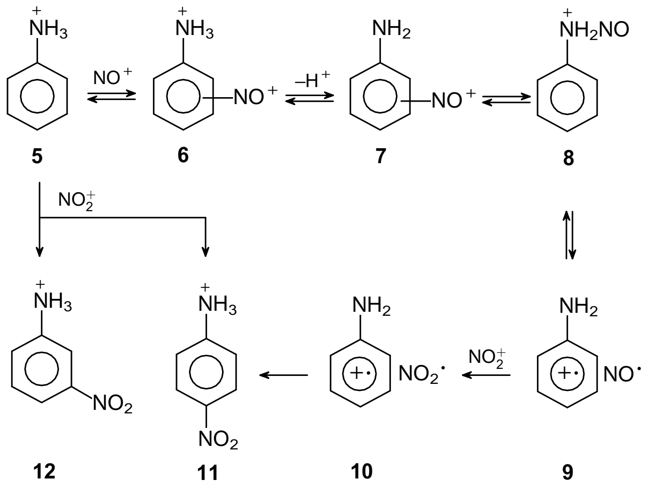
[†] *Selected spectroscopic data.* ^{13}C NMR (90 MHz, 100% H_2SO_4) δ_{TMS}: $PhNH_3^+$ 122.66 (C-2, C-6), 127.61 (C-1), 130.72 (C-4), 130.84 (C-3, C-5); *p*-$NO_2C_6H_4NH_3^+$ 125.42 (C-2, C-6), 126.59 (C-3, C-5), 134.63 (C-1), 148.12 (C-4); *m*-$NO_2C_6H_4NH_3^+$ 119.52 (C-2), 126.19 (C-4), 129.51 (C-1), 130.96 (C-6), 132.53 (C-5), 148.20 (C-3); PhN_2^+ 112.82 (C-1), 132.26 (C-2, C-6), 132.60 (C-3, C-5), 143.12 (C-4); *p*-$NO_2C_6H_4N_2^+$ 119.67 (C-1), 127.60 (C-3, C-5), 134.51 (C-2, C-6), 154.28 (C-4); *m*-$NO_2C_6H_4N_2^+$ 115.73 (C-1), 125.69 (C-2), 134.59 (C-5), 137.28 (C-4), 137.81 (C-6), 148.43 (C-3).

[‡] The ratio of nitro isomers was determined by TLC of azo compounds (Silufol UV-254, benzene–hexane, 3:4) and spectrophotometry in $CHCl_3$, λ_{max} 493.3 nm (*p*-nitro) and 450.7 nm (*m*-nitro), or by the relationship between integral intensities in the ^{1}H NMR spectra of nitroanilinium ions on reaction in 100% H_2SO_4 and of nitrobenzenediazonium ions on reaction in 92–95% H_2SO_4. Values of the *para*/*meta* ratio obtained in the absence of $NO^+HSO_4^-$ were close to the data in ref. 5.

rate of aniline diazotisation, examined up to 74% sulfuric acid acidity,[6] decreases owing to hindrance to proton loss from *N*-nitrosoanilinium ion. According to our results, at far greater acidity it falls to zero.

Increasing *para*-substitution in nitration in the presence of nitrosonium hydrogensulfate may be interpreted as catalysis by nitrous acid in the reaction of primary aromatic amine, found earlier for nitration of tertiary amine *N*,*N*-dimethylaniline.[9] By analogy, one should propose the rate determining formation of ion-radical pair **9** from *N*-nitrosammonium ion **8** followed by attack with nitronium ion to give ion-radical pair **10**. Subsequent steps involving association of the radicals in species **10** and aromatization of the σ-complex lead to the *para*-nitro derivative **11**. Formation of the exclusively *para*-nitro isomer in catalysed nitration of anilinium ion is confirmed by analogy both with catalysed *para*-nitration of *N,N*-dimethylanilinium ion[5] and with regioselective *para*-bromination of anilinium ion in the presence of nitrosonium ion in concentrated sulfuric acid.[10] Concurrent uncatalysed nitration of anilinium ion provides *meta*-nitro **12** and *para*-nitro **11** derivatives in the ratio typical of nitration in the absence of diazotising agent.[5] On this assumption it follows from the data in Table 1 that the proportion of catalysed and uncatalysed reaction paths are approximately equal in the presence of 1 mol of nitrosonium hydrogensulfate in 92% sulfuric acid.



Scheme 2

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