Acid-catalysed disproportionation and benzidine rearrangement of phenylhydrazinopyridines: reaction pathways, kinetics and mechanism[1]

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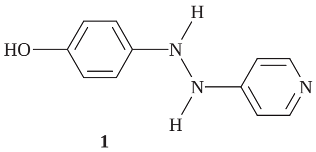
A kinetic and product analysis study of the reaction of 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine (1) and 4-(*N*′-phenylhydrazino)pyridine (2) in 10–55 wt% aqueous sulfuric acid media is reported. The final products obtained from 1 are the oxidation product, 4-(4-hydroxyphenylazo)pyridine (3), and the two reduction products 4-aminophenol and 4-aminopyridine. This product pattern resembles that of the disproportionation products observed in some cases of the benzidine rearrangement. The reaction of 2 gives a complex product mixture including the disproportionation products 4-(phenylazo)pyridine (4), aniline and 4-aminopyridine, and other benzidine-type products including a *p*-semidine. Complicating the situation is the concurrent hydroxylation and disproportionation of 4 which take place in these media, giving 3, 4-aminopyridine and 4-aminophenol. The observed pseudo-first-order rate constants for the disproportionations increase steeply with acid concentration without showing any downturn at higher acidities. The disproportionation rate constants for 1 and 2 are much larger than those for the hydroxylation of 4. A reasonable mechanism which explains the observations is a benzidine-type rearrangement with accompanying disproportionation. To our knowledge this work is the first description of this type of reaction in substrates containing pyridinium rings.

Azo, azoxy and hydrazo dye molecules have continued to provide fertile ground for important discoveries having both practical and theoretical significance. The wide range of mechanistic variety and structure–activity relationships that we have observed in our studies of azo and azoxy arenes[2–5] reached an unexpected turn with the discovery disclosed in the previous paper,[6] that 4- and 2-(phenylazo)pyridine are both unstable in aqueous acid media, undergoing hydroxylation of the aromatic nucleus with concurrent aminophenol and aminopyridine formation. These processes—oxidation and reduction—are reminiscent of the disproportionation which accompanies the classical benzidine rearrangement of some hydrazoarenes.[7–9] Evidence was presented that the hydroxylation of a phenylazopyridine involves formation of a phenylhydrazinopyridine as a transient reaction intermediate, which subsequently undergoes fast disproportionation to the observed oxidized and reduced products.[6]

In the present work we have synthesized the surmised intermediate, 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine **1**, as well as 4-(*N*′-phenylhydrazino)pyridine **2**, and subjected them to the acid media used in the former study[6] in order to determine the products and evaluate the kinetics. Our study has revealed a sequence of reactions. For instance, starting with **2** there is an initial disproportionation to 4-(phenylazo)pyridine (oxidation), and aniline and 4-aminopyridine (reduction). This is followed by hydroxylation of the 4-(phenylazo)pyridine to **1** and, finally, another disproportionation of **1** to 4-(4-hydroxyphenylazo)-pyridine (oxidation), and 4-aminophenol and 4-aminopyridine (reduction). Based on the kinetic study, a reaction profile is presented for this sequence of processes. A mechanism akin to the classical benzidine rearrangement,[7,10,11] is proposed for these systems.



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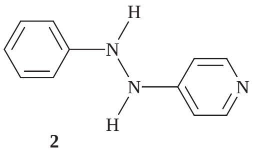

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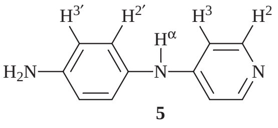
Experimental

4-[*N*′-(4-Hydroxyphenylhydrazino]pyridine **1** and 4-(*N*-phenylhydrazino)]pyridine **2** were synthesized by a method similar to that used for the preparation of hydrazinobenzene.[12] Highly reactive diimide was generated *in situ* by the cupric ion-catalysed oxidation of hydrazine with hydrogen peroxide. The corresponding azo compounds, 4-(4-hydroxyphenylazo)-pyridine (**3**) and 4-(phenylazo)pyridine (**4**), were then reacted with diimide giving, respectively, **1** in 33.0% yield, mp 258–259 °C, and **2** in 69.4% yield, mp 170–171 °C (lit.[13] 171–172 °C). All the compounds synthesized were characterized by a combination of ^1H and ^{13}C NMR, UV and mass spectroscopic methods as before.[6]

Compounds and products were purified by several techniques, recrystallization, column and thin layer chromatography (TLC) using silica gel 60 F_{254} plates (BDH) in various eluting solvent systems. The products of the reactions of **1** and **2** in 65 wt% aq. H_2SO_4 were identified by direct isolation as previously described.[6] The structural identification of the semidine **5**, formed during the reaction of **2**, was achieved using ^1H NMR spectroscopy and MS: δ_H([$^2H_6$]DMSO) 8.05 (d, H^2), 8.01 (s, H^α), 6.61 (m, $H^{2'}$, $H^{3'}$), 6.55 (d, H^3), 4.95 (br s, NH_2); *m*/*z* 185 (M^+).



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The kinetic techniques used were similar to those previously described.[6]

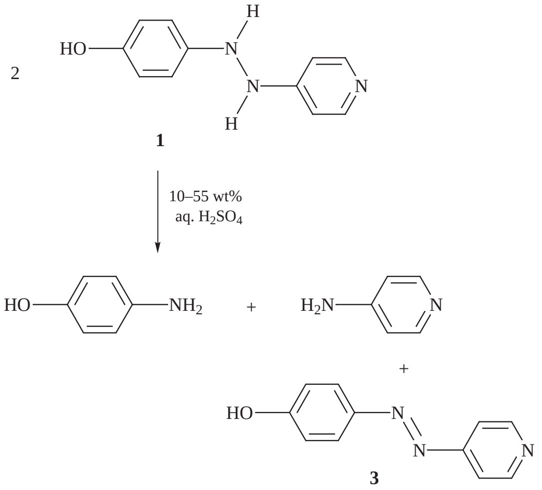
Results

Products

All of the products identified when **1** and **2** react at a substrate concentration of ~0.05 M in aqueous 65 wt% sulfuric acid are given in Schemes 1 and 2, respectively. The yields of each product, and of the several by-products observed, are given in

Table 1 Isolated products and yields in the reactions of **1** and **2** in 65 wt% H_2SO_4

Substrate	Product	Yield (%)	Total yield (%)
1	4-(4-Hydroxyphenylazo)pyridine **3**	26	72
	4-Aminopyridine	22	
	4-Aminophenol	24	
2	4-(Phenylazo)pyridine **4**	9	75
	4-Aminopyridine	15	
	Aniline	8	
	4-(4-Hydroxyphenylazo)pyridine **3**	5	
	4-Aminophenol	7	
	Dimeric product	6	
	p-Semidine product **5**	6	
	Unknown products	19	



Scheme 1

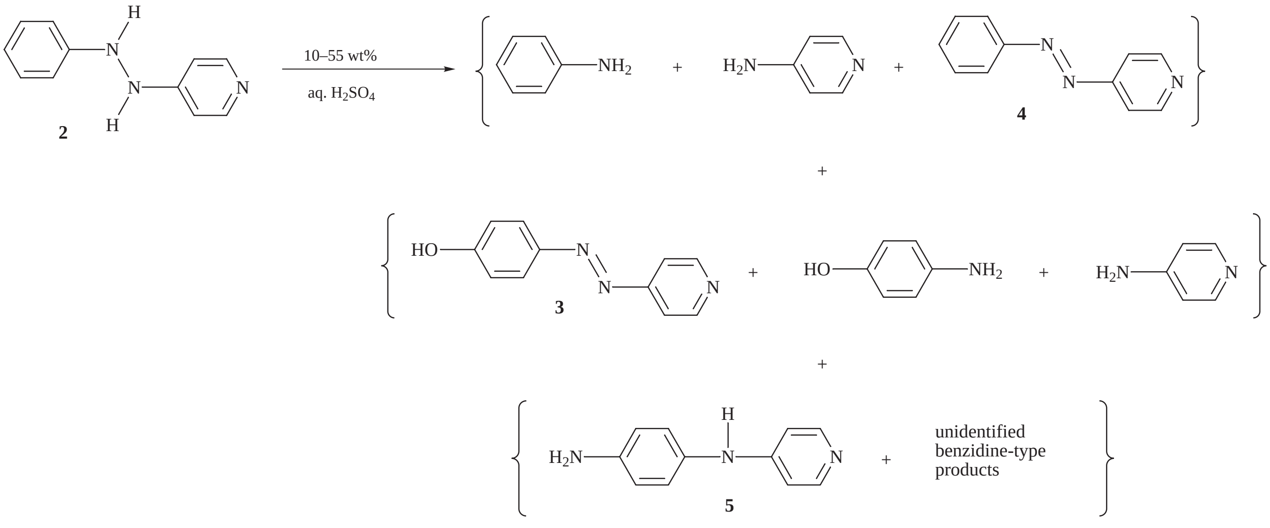
Table 1. For the reaction of **1**, the yield of **3** could be calculated directly from the final UV–VIS spectra obtained during the kinetic runs, using the known extinction coefficient; this proved to be independent of the sulfuric acid concentration, averaging 43.8 ± 2.5% over the range 32–86 wt% H_2SO_4, and of the substrate concentration, averaging 49.1 ± 2.0% over the range $1–8 \times 10^{-5}$ M in 32.59 wt% H_2SO_4. The yields of 4-aminophenol and 4-aminopyridine could not be calculated directly, but as Table 1 shows, undoubtedly form in equivalent yields. Evidently the reaction is uncomplicated, two moles of **1** giving one mole of oxidized and one of reduced products (with the N–N bond broken).

The situation with **2**, shown in Scheme 2, is more complex, however. Apart from disproportionation products similar to those formed from **1** (including **4**, bracketed together in Scheme 2), products are formed from **4** as it too reacts under these conditions;[6] these products are also bracketed together in Scheme 2. In addition, benzidine rearrangement-type products are formed, of which only **5** could be conclusively identified, the others being impossible to separate by TLC. GC–MS analysis showed them to have different GC retention times, but the same molar mass as **5**, strengthening their identification as rearrangement products. The percentage yield of one of the disproportionation products, **4**, could be obtained from the final UV–VIS kinetic scans; this proved to be independent of the sulfuric acid concentration, being 6.59 ± 0.86% over the 10–60 wt% H_2SO_4 concentration range, at a substrate concentration of 8.4×10^{-5} M. This low value means that the pathway leading to the benzidine rearrangement-type products is the more important one, perhaps by a factor of 2–3.

Kinetics

The kinetics of the disproportionation of **1** and **2** were followed spectrophotometrically by monitoring the formation of the corresponding azo products, **3** at 408 nm and **4** at 340 nm. The range of sulfuric acid concentrations used for **1** and **2** was 10–55 wt% H_2SO_4; beyond 55 wt% the disproportionation of **1** was too fast (half-life < 4 s) to follow using our equipment. For **1** in 32.59 wt% H_2SO_4 the rate constants were independent of substrate concentration over the $1–8 \times 10^{-5}$ M range, showing the reaction to be accurately first-order, and over this range the rate constant for substrate removal, $(10.15 \pm 0.49) \times 10^{-3}$ s^{-1}, was identical with that for product formation, $(9.98 \pm 0.45) \times 10^{-3}$ s^{-1}, showing that no intermediates accumulate during the disproportionation. Reactions were generally followed over three half-lives, and all showed excellent first-order behaviour over this range. The observed pseudo-first-order rate constants, k_ψ, are given for **1** in Table 2 and for **2** in Table 3, together with other pertinent information. The rate data are plotted as a function of wt% H_2SO_4 in Fig. 1.

These rate data were treated according to the excess acidity method.[14] To this end, plots of $\log k_\psi - \log C_{H^+}$ *vs.* X for all three substrates are shown in Fig. 2. The log proton concentrations C_{H^+} and the excess acidities X were obtained from published sources.[15] Straight lines are drawn through the data in Fig. 2; for **1** the slope is 0.806 ± 0.024 and the intercept is −3.702 ± 0.039, and for **2** the slope is 0.684 ± 0.066 and the intercept −4.65 ± 0.10. Unfortunately Fig. 2 is compatible with any of the possible acid-catalysis mechanisms, A1, A2 or A-S_E2.[14] The slopes are shallow, characteristic of rate-determining proton transfer (A-S_E2);[14] this would be slow



Scheme 2

Table 2 Kinetic data for 4-[*N*′-(4-hydroxyphenylhydrazino)pyridine (**1**)

H_2SO_4 (wt%)	$k_\psi/10^{-3}$ s^{-1} [a]	X [b]	$\log C_{H^+}$ [b]	$\log k_\psi - \log C_{H^+}$
10.11	0.323	0.234	0.123	−3.614
	0.325			−3.611
20.13	2.04	0.578	0.464	−3.154
	1.76			−3.218
32.59	9.16	1.179	0.718	−2.756
	8.84			−2.772
36.73	21.1	1.421	0.782	−2.458
	20.2			−2.477
43.80	56.2	1.884	0.876	−2.126
	51.8			−2.162
45.75	73.5	2.023	0.900	−2.034
	74.6			−2.027
49.55	124.1	2.309	0.942	−1.848
	118.5			−1.868
53.69	217.3	2.648	0.984	−1.647
	209.5			−1.663

[a] Observed pseudo-first-order rate constants; both duplicate determinations given. [b] From ref. 15.

Table 3 Kinetic data for 4-(*N*′-phenylhydrazino)pyridine (**2**)

H_2SO_4 (wt%)	$k_\psi/10^{-3}$ s^{-1} [a]	X [b]	$\log C_{H^+}$ [b]	$\log k_\psi - \log C_{H^+}$
10.11	0.040	0.234	0.123	−4.521
20.13	0.190	0.578	0.464	−4.185
32.59	0.810	1.179	0.718	−3.810
43.80	2.14	1.884	0.876	−3.546
53.69	17.4	2.648	0.984	−2.743

[a] Observed pseudo-first-order rate constants. [b] From ref. 15.

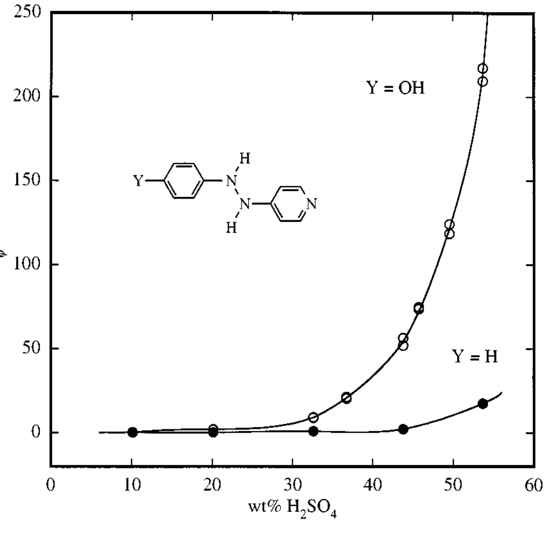


Fig. 1 Rate constants for the reactions of **1** (○) and **2** (●) as a function of sulfuric acid concentration

transfer of a proton to the monoprotonated substrate, since protonation on the pyridine nitrogen takes place in the pH range for these substrates.[5] On the other hand, despite the straight lines drawn the data may be better described by downward curves, particularly if the last point on the Y = H line is in error. Two factors may cause downward curvature in this type of plot, reaction of water with the protonated reactant in the slow step (A2),[14] or the presence of a substrate p*K* value in the acid range covered by the rate measurements in an A1 reaction.[14] The first of these, reaction of the monoprotonated substrate with water, seems unlikely, but the latter seems reasonable. Steep slopes would be expected at low acidities before substrate diprotonation is complete (*i.e.* slopes of 1 + 0.81 for **1** and 1 + 0.68 for **2**), and shallower slopes after that, if the substrate is mostly fully diprotonated in the acidity range covered by the rate measurements.[14] Thus the second proton transfer may be part of the rate-determining step, or it may be a pre-equilibrium process; based on the evidence of Fig. 2 a decision between these two is not possible.

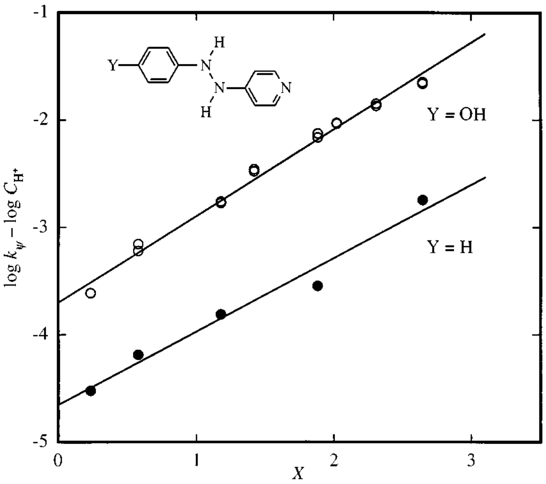


Fig. 2 Excess acidity plots of $\log k_\psi - \log C_{H^+}$ *vs.* X for the reactions of **1** (○) and **2** (●) in aqueous sulfuric acid

Discussion

Reaction pathways

Reaction of 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine, 1. Disproportionation is known to accompany the benzidine rearrangement in the acid-catalysed reactions of hydrazinoaromatics.[7–9] In particular, disproportionation becomes a major pathway with 4,4′-disubstituted hydrazobenzenes, leading to one oxidized product (the azo compound) and two reduced products (two anilines).[7,9]

In the present study it has been found that the reaction of 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine (**1**) gave the azo product 4-(4-hydroxyphenylazo)pyridine (**3**) in 26% yield, and two amines, 4-aminopyridine and 4-aminophenol, in 22 and 24% yields, respectively (Table 1), these yields remaining constant over a range of acid concentrations (see Experimental section). This is the characteristic product distribution formed from the disproportionation of hydrazo aromatics.[9] Thus the product distribution found for the reaction of **1** indicates that only disproportionation is occurring. In the accompanying study[6] we have found that **1** is involved as the central intermediate in the reaction of 4-(phenylazo)pyridine (**4**) in aqueous sulfuric acid (Scheme 3). It was proposed that hydroxylation (k_h) is the slow step since **1** was not observed spectrally in the repetitively scanned UV–VIS spectra in the reaction of **4**; if hydroxylation (k_h) was fast and disproportionation (k_d) was the rate-determining step, then the hydrazo intermediate would accumulate and be spectrally observable.

The present study provides a confirmation of this proposal (Scheme 3), since the rate constants for disproportionation (k_d) could be determined with authentic 4-[*N*′-(4-hydroxyphenylhydrazino)]pyridine (**1**). The kinetic behaviour as a function of acid concentration for **1** is shown together with that for 4-phenylazopyridine (**4**) in Fig. 3; this shows a steep increase for **1**, but a much slower process with a bell-shaped profile and a rate maximum at 72 wt% H_2SO_4 for **4**. The rate constant for disproportionation (k_d) is at least 150 times greater than that of the hydroxylation (k_h). This large rate difference accounts for the fact that **1** is not observed spectrally in the reaction of **4**.[6]

Reaction of 4-(*N*′-phenylhydrazino)pyridine, 2. Since we have found that **1** gives rise to the corresponding azo product **3** *via* disproportionation, it follows by analogy that **2** is the precursor in the formation of **4**. To confirm this we have investigated the

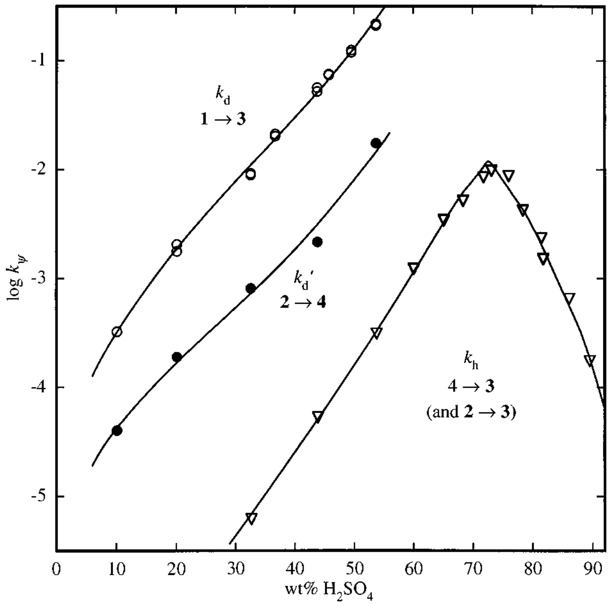
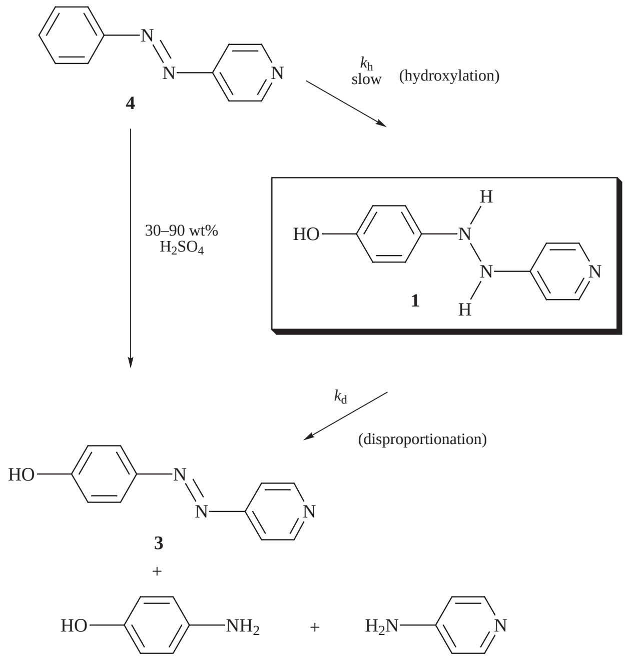


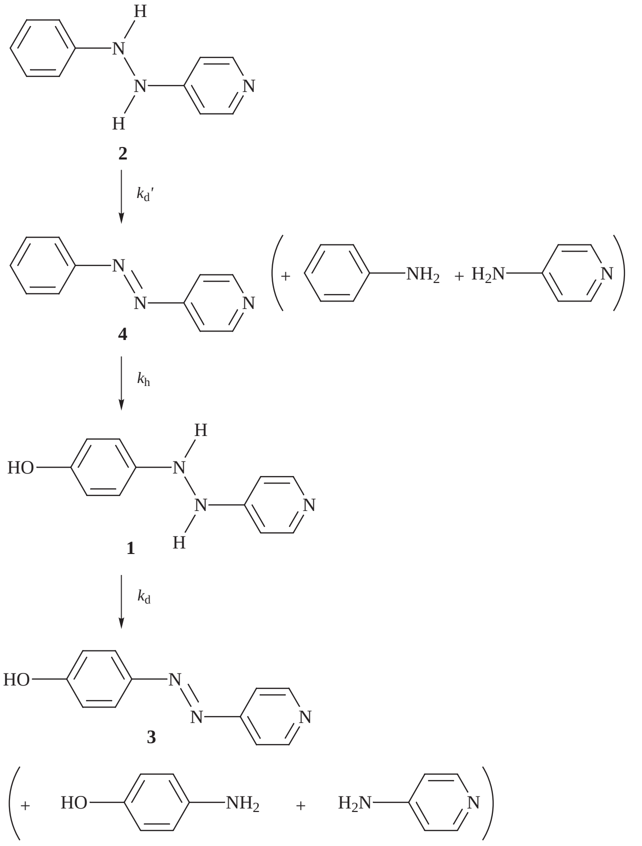
Fig. 3 Plots of log k_ψ *vs.* the sulfuric acid concentration for the reactions **1**→**3** (○), **2**→**4** (●) and **4**→**3** (with **2**→**3**) (△), allowing rate comparisons. Data for the latter process were obtained from ref. 6.



Scheme 3

reaction of **2** in aqueous H_2SO_4. As expected, it was found that **2** underwent disproportionation to form **4**, together with two amine products. However, in the reaction of **2** a competing benzidine-type rearrangement occurred as well, being responsible for the formation of a complex range of products (Scheme 2; Table 1) including a semidine (**5**). The overall reaction pathway **2**→**4** in the reaction of **2** is illustrated in Scheme 4. In Fig. 3 are displayed three rate profiles as a function of acid concentration corresponding to the measured rate constants for four processes; k_d' is the rate constant for **2**→**4**, k_d for **1**→**3**, and k_h for **4**→**3** and **2**→**3**.

Based on the kinetic behaviour of each process given in Fig. 3, a qualitative energy profile for the overall process **2**→**3** can be constructed as in Scheme 5, where the acidity region for the kinetic measurements of each process is also given. Thus **2** gives rise to **4** *via* disproportionation (k_d'), which then undergoes hydroxylation (k_h), the slow step, **4**→**1**. On the other hand, starting with **4** as the reactant, the **4**→**3** process involves formation of the hydrazo species **1** as an intermediate which then undergoes disproportionation (k_d) to produce the final azo product **3** and two anilines. The rate profiles reflect the fact that the activation barrier for the **4**→**1** process will be the highest, while the energy barrier for the **1**→**3** process will be the lowest as shown in Scheme 5. This is in accord with the rate profiles in Fig. 3 which show a similar pattern for two disproportionation processes **2**→**4** and **1**→**3**, *i.e.* reaction in the low acid region and a step increase with acidity, while the two hydroxylations **2**→**3** and **4**→**3** require much higher acidities and exhibit nearly coincident bell-shaped curves. Since the rates of the two disproportionation steps **2**→**4** and **1**→**3** are much greater than the hydroxylation step **4**→**1**, the rate constants for the two processes **2**→**3** and **4**→**3** will correspond to that of the slowest step, *i.e.* **4**→**1**. Hence the rate profiles for the two processes **2**→**3** and **4**→**3** are almost coincident, as found in Fig. 3. Also in accord with the profile in Scheme 5 is the observation that with **2** as the reactant in the high acid concentration regime (60–90 wt% H_2SO_4), there is immediate formation of **4**, followed by its slow transformation to **3**. However, **1** is an unobservable transient intermediate when starting with **2** or **4** as the reactant.

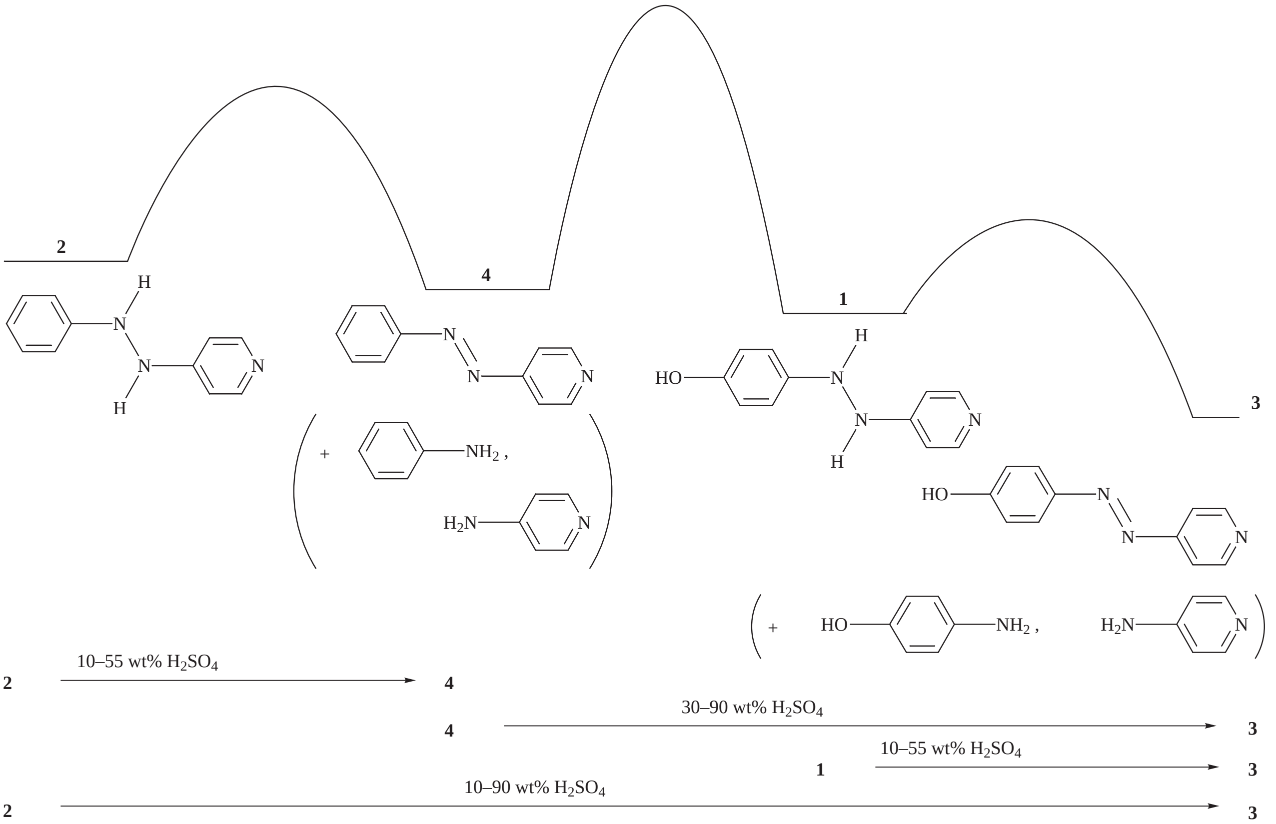


Scheme 4

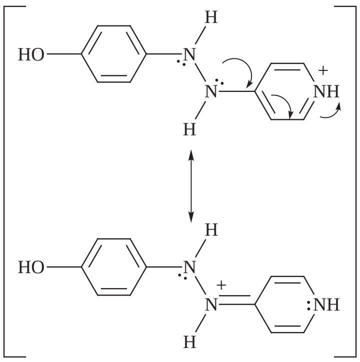
Kinetics and mechanism

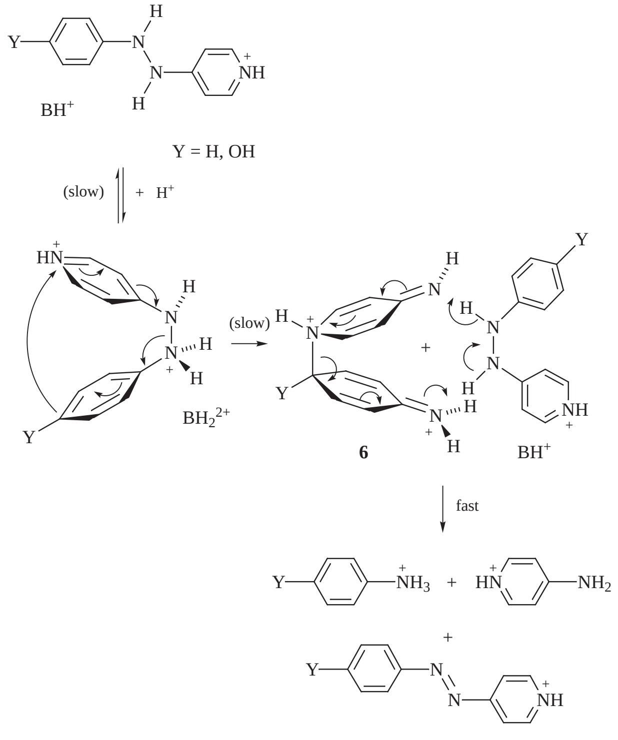
Proposed mechanisms for these disproportionation reactions have to account for the observed products and the observed kinetic behaviour, which is that a second proton transfer is involved. This may be part of the rate-determining step, or it may be a pre-equilibrium to an A1 process involving the diprotonated substrate. The second protonation is likely to be on the hydrazino nitrogen away from the pyridinium ring. There are two reasons for this: apart from simple electrostatic repulsion of the two positive charges the lone pair on the other nitrogen is occupied to some extent in resonance interaction with the pyridinium centre, as shown below, and thus is less available for protonation.

We propose the benzidine rearrangement-type mechanism shown in Scheme 6 as being the most likely mechanism for the



Scheme 5

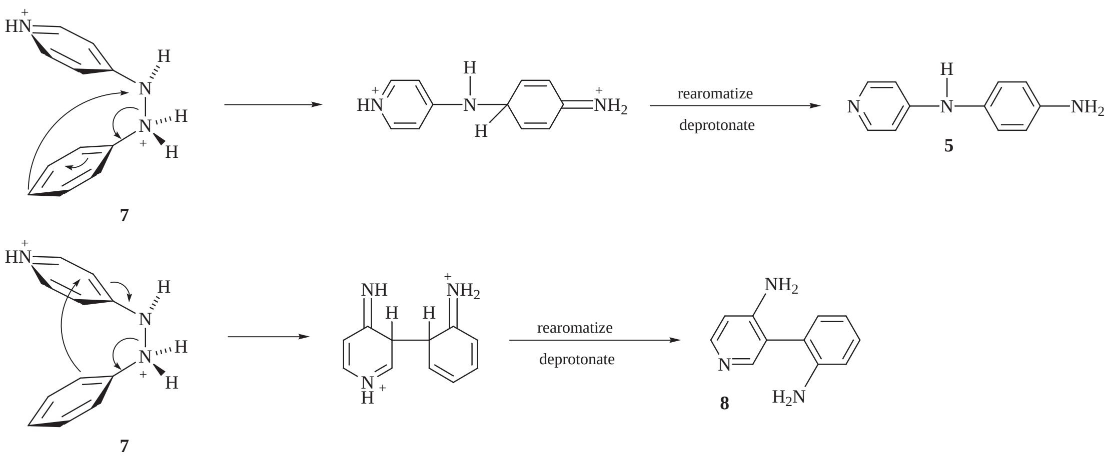




Scheme 6

reaction of **1** and **2**; it predicts the correct products. The rate-limiting step may be an A1 rearrangement of BH_2^{2+}, with the initial proton transfer being a pre-equilibrium process, or the proton transfer could be part of the rate-determining step, probably concerted with the rearrangement process. The rate-determining step is (or includes) a thermally allowed 10-electron electrocyclic reaction,[11] which is now firmly established as being the rearrangement mechanism for hydrazinobenzene and many other hydrazino aromatics, primarily by the application of heavy-atom isotope effect studies to these processes.[7,11] Also, for hydrazinobenzene itself, an intermediate equivalent to **6** has been experimentally observed under stable-ion conditions.[16] Regular hydrazino compounds can form benzidines by rearomatization of intermediates like **6**, but this cannot happen here because the pyridine nitrogen would have to acquire a permanent positive charge (and because of the presence of the OH for **1**). Because of this, disproportionation is much more probable, and the reaction with another BH^+ molecule is proposed by analogy with a similar proposal made for the disproportionation of 4,4′-diiodohydrazinobenzene.[7,9] This is likely to be quite a fast reaction, because (a) it is a highly favourable, thermally allowed 14-electron electrocyclic reaction, (b) it is energetically downhill because the aromatic protonated products formed are all much more stable than is **6** in the reaction medium and (c) formation of three molecules from two counteracts the entropy factor involved in orienting **6** and BH^+ for reaction.

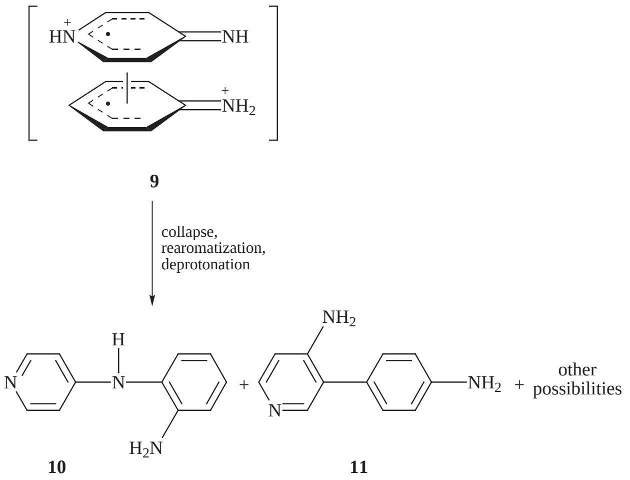
Evidently other benzidine rearrangement processes are not very important for **1**; Table 1 shows that Scheme 6 accounts for almost all of the reaction products, no other rearrangement products being detected. However, this is not the case for **2**, where **5** and other unidentified rearrangement products were



Scheme 7

detected in addition to the products already discussed. Also **2** has an open *para* position, which makes other ring closures seem more likely, so it is worth examining the other possibilities for this molecule. The two possible thermally allowed six-electron electrocyclic reactions are shown in Scheme 7. Closure of the open *para* position of **7** to the unprotonated nitrogen leads to the observed *p*-semidine product **5**, and closure of two *ortho* positions gives the *o*-benzidine product **8**, which is probably one of the unidentified benzidine products observed.

Other benzidine products cannot arise by thermally allowed electrocyclic processes, and a π-complex mechanism is usually invoked to account for them.[2,7,10] If we write the N–N bond as undergoing homolysis, π-complex **9** results, shown in Scheme 8. (Heterolysis leads to structures which have both positive charges on the same ring segment.) This can couple in many different ways, for instance, Scheme 8 shows *o,N* and *o,p* coupling to give two commonly observed rearrangement products, *o*-semidine **10** and diphenylene **11**. However, we have no evidence as to whether or not this is occurring with our substrates. The predominant disproportionation we observe is one indication that at least most of our products arise from electrocyclic reactions.



Scheme 8

In the previous study[6] we found that in the reaction of **4** to **3** (*via* **1**) the yield of **3** varied with the medium acidity, remaining constant at 40–50% up to ~72 wt% H_2SO_4, and then decreasing steadily to 12% in 86 wt% H_2SO_4. With a likely mechanism for the formation of **3** proposed (Scheme 6) we can now see why this should be. For the disproportionation to **3** to occur there must be monoprotonated BH^+ present to react with **6**, but as the acidity increases BH^+ becomes diprotonated to BH_2^{2+}, and the increased electrostatic repulsion between **6** (with two positive charges) and BH_2^{2+} will make this process less favourable. This means that alternate benzidine rearrangement pathways from **6** will become more likely relative to the disproportionation at the higher acidities, decreasing the yield of **3**. This seems reasonable. We observed above that for **2** rearrangement products are formed two to three times faster than disproportionation products over a range of sulfuric acid concentration. Unlike **2**, **1** has a *p*-hydroxy substituent, making rearrangement to the *para* position improbable, but products equivalent to **8** and **10** can still form.

The benzidine rearrangement of hydrazinobenzenes is a fast reaction.[2] Our reactions are quite fast, but rate comparisons are difficult because most other kinetic studies have been performed in dilute acid media containing a co-solvent, and the acid used is usually HCl or $HClO_4$ rather than H_2SO_4.[2] The most recent study is that of Bunton and Rubin,[17] who studied hydrazinobenzene (*i.e.* 1,2-diphenylhydrazine) and two substituted hydrazinobenzenes in pure aqueous HCl and $HClO_4$ to concentrations of about 1 M; their substrates were diprotonated (on both hydrazo nitrogens), and their reaction rates were much faster than ours, in the stopped-flow range.

Depending on the substrate, the hydrazo group may be diprotonated, monoprotonated or even unprotonated during the rearrangement step, but the process is fastest for diprotonated substrates and slowest for unprotonated ones.[2,7,17] Our substrates are diprotonated but one of the protons is on the pyridine nitrogen; because of this, protonation on the other hydrazino nitrogen (to give a triprotonated species) is expected to be very difficult, only occurring at acidities much higher than those used here. Diprotonation in hydrazinobenzenes is assumed to speed the reaction by encouraging N–N bond cleavage and the subsequent charge separation.[2] Hydrazino group protonation presumably has this effect here too, but since the two positive charges are further apart in our case the reaction will not be accelerated nearly so much, which probably accounts for our rates being slower than those of Bunton and Rubin.

Mechanisms are sometimes suggested for the benzidine rearrangement in which the second proton transfer is part of the rate-determining step (A-S_E2 mechanism), as could be the case here. For instance rate-limiting ring carbon protonation followed by fast N–N bond cleavage[16] was a popular proposed mechanism at one time,[2] as was rate-determining formation of the $-\overset{+}{N}H_2-\overset{+}{N}H_2-$ species with its subsequent rearrangement being a fast process.[17] More recent heavy-atom isotope effect results[18] have rendered these mechanisms less likely, however.[7]

The benzidine rearrangement has always fascinated chemists, and interest in it continues to be high.[2,7–11] For instance an 18-electron thermally allowed electrocyclic reaction in a benzidine rearrangement has been described very recently,[19] which complements the 6-, 10- and 14-electron processes discussed in this work. A variety of substrates for the reaction has been used over the years, but to our knowledge this work is the first description of benzidine rearrangement-type processes in substrates containing pyridinium rings.

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