Kinetics and Mechanisms of the Bamberger Rearrangement. Part 3.† Rearrangement of Phenylhydroxylamines to *p*-Aminophenols in Aqueous Sulphuric Acid Solutions

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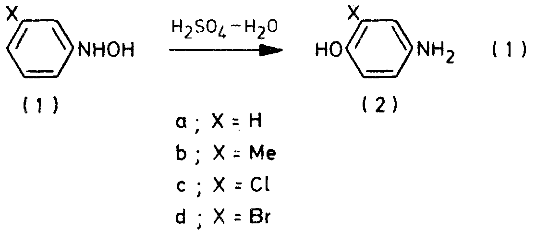
The rates of Bamberger-type rearrangement of phenylhydroxylamine (1a) and its derivatives (1b—d) to the corresponding *p*-aminophenols were determined in sulphuric acid solution. Plots of the pseudo-first-order rate constants against pH (or H_0) indicate that the active species at [H_2SO_4] < 1.00N (pH region) is the *O*-protonated arylhydroxylamine ($ArNHO^+H_2$) which exists in equilibrium with the *N*-protonated species (ArN^+H_2OH), while the diprotonated species ($ArN^+H_2O^+H_2$) contributes significantly to the observed reaction rate at [H_2SO_4] > 1.00N (H_0 region). The slope of Hammett plots (ρ) which was obtained by plotting k_{obs} at [H_2SO_4] 1.00N against the Hammett σ values was −3.19. It was also established that the $\Delta S^‡$ values for the four substrates are all positive. These results suggest that the Bamberger rearrangement occurs by an S_N1 mechanism and that the elimination of water from $ArNHO^+H_2$ is rate determining.

IN 1894, BAMBERGER[1] reported that phenylhydroxylamine (1a) readily rearranges to *p*-aminophenol (2a) [reaction (1)] in sulphuric acid solution. The reaction has since been employed as a convenient method to synthesize *para*-substituted anilines, for example, *p*-aminophenol, *p*-halogenoanilines, and *p*-alkoxyanilines can be formed *in situ* by reduction of nitrobenzene.[2-5] On the other hand, the reaction mechanism has escaped attention. Yukawa[4] proposed an S_N2 mechanism, while Ingold *et al.*[6] claimed that an S_N1 mechanism is more feasible but the S_N2 mechanism cannot be ruled out. The only certainty was that the reaction occurs through intermolecular rearrangement on the basis that treatment of (1a) in $H_2{}^{18}O$–H_2SO_4 provides ^{18}O-incorporated (2a).[7] Apart from this, almost nothing is known about the reaction mechanism. In fact, no previous kinetic investigation has been carried out. We here report the first, detailed kinetic investigation of the Bamberger-type rearrangement of (1a) and its derivatives and discuss the reaction mechanism on the basis of pH dependence, substituent effects, and thermodynamic parameters.



RESULTS AND DISCUSSION

Absorption Spectra and Protonation Equilibria of Phenylhydroxylamines.—A spectral study indicated that phenylhydroxylamine (1a) is converted predominantly into *p*-aminophenol (2a) and in part into nitrosobenzene (3a) and azoxybenzene (4a). As the reaction was very rapid, it was almost impossible to measure the absorption spectra of (1a) accurately. In order to determine the spectral shape of (1a), we measured the optical densities at various wavelengths as a function of time and extrapolated the time-dependent optical densities back to zero time. The spectra thus depicted are recorded in Figure 1. The spectrum of (1a) in water showed an absorption maximum at 277 nm (ε 950). It decreased with increasing sulphuric acid concentration and became unaffected at sulphuric acid concentrations <1.00N. This result means that the spectrum in water can be attributed to the free base (PhNHOH) and that in 1.00N-sulphuric acid to the conjugate acid (PhN^+H_2OH). The pK_a value of (1a) was calculated from the absorption at 280 nm where the intensity of PhN^+H_2OH is almost negligible by comparison with that of PhNHOH. The pK_a values for the *meta*-substituted phenylhydroxylamines (1b—d) were also estimated in the same manner (Table 1). A plot of pK_a against Hammett values σ_m[8] provided a good linear relationship (r > 0.998), the reaction constant (ρ) being −2.57. The magnitude is

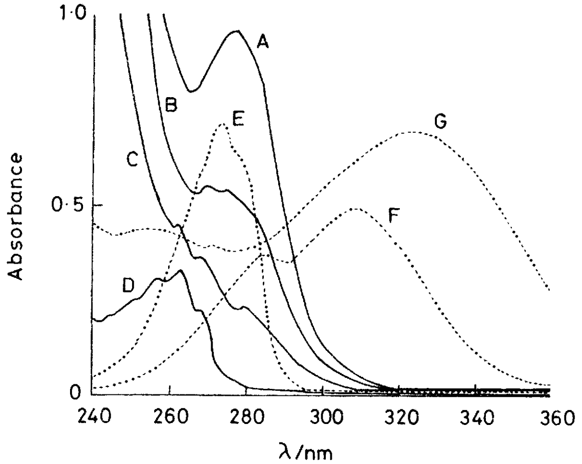


FIGURE 1 Absorption spectra of PhNHOH (A–D; 1.00mM), p-$HOC_6H_4NH_3^+$ (E; 0.50mM), PhNO(F; 0.05mM), and PhN(O)NPh (G; 0.05mM). (A) in H_2O, (B) in 0.01N-H_2SO_4, (C) in 0.05N-H_2SO_4, and (D) in 1.00N-H_2SO_4

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† Part 2 is ref. 5*b*

comparable with that obtained from a plot for substituted anilines (−2.77).[9]

Kinetic Studies.—The rearrangement of (1a) to (2a) was followed by monitoring the absorption band of *p*-hydroxyanilinium ion at 273 nm. It was found on the basis of the spectral examination (see Figure 1) that the yields of (3a) and (4a) increase with increasing pH of the medium, amounting to *ca.* 10% in the extreme case. In cases where the undesired by-products were detected spectrophotometrically, the optical densities were corrected for these materials. On the other hand, these by-products were almost undetected at $[H_2SO_4] > 1.00$N. The observation suggests that the free base of (1a) is oxidized by air to give (3a), which is further converted to (4a) by acid-catalysed condensation.

TABLE 1

pK_a Values of phenylhydroxylamines (1a—d) at 40.0 °C

Substrate	pK_a
(1a)	1.90
(1b)	2.15
(1c)	1.00
(1d)	0.92

$$\underset{(1a)}{\mathrm{PhNHOH}} \xrightarrow{O_2} \underset{(3a)}{\mathrm{PhNO}} \xrightarrow[H^+]{(1a)} \underset{(4a)}{\mathrm{PhN(O)NPh}} \qquad (2)$$

First-order plots for the rearrangement reaction were linear up to 60% reaction at least, and the first-order rate constants (k_{obs}) determined from the initial slopes were independent of the initial concentration of (1a) (0.500—6.00mM). Plots of k_{obs} *versus* pH (or H_0) [10] (Figure 2) indicate that k_{obs} increases with decreasing pH and become almost constant between pH 1 and H_0 −1. Interestingly, we found that k_{obs} further increases at $H_0 < -1$. The plots for (1b—d) also provided similar pH–rate profiles.

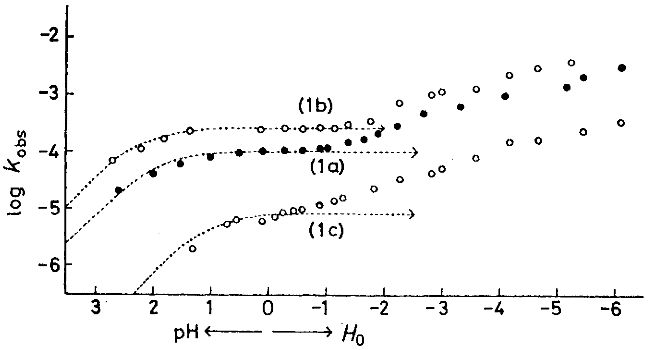
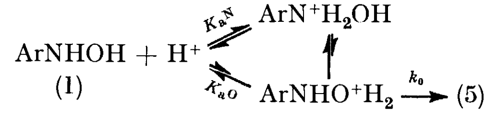


FIGURE 2 log k_{obs} against pH or H_0 for the rearrangement of *m*-substituted phenylhydroxylamines at 40.0 °C

The fraction of *N*-protonated phenylhydroxylamines is given by equation (3). If the active species at pH > 0 is the *N*-protonated species, k_{obs} can be expressed by equation (4) where K_a^N and k_N are the acid dissociation constant and the rate constant, respectively, for ArN^+H_2OH and k_N is the plateau value of k_{obs}. As shown in Figure 2, the theoretical curves (dotted lines) well explained the experimental plots. Previously, Ingold *et al.*[6] proposed the mechanism in Scheme 1 for the Bamberger-type rearrangement. The mechanism involves the *O*-protonated species as an obligatory intermediate. The kinetic equation for Scheme 1 is given by equation (5), which is essentially equivalent to equation (4).

$$[ArN^+H_2OH] = [H^+][(1)]_{total}/(K_a^N + [H^+]) \qquad (3)$$

$$v_{obs} = k_{obs}[(1)]_{total} = k_N[ArN^+H_2OH] = k_N[H^+][(1)]_{total}/(K_a^N + [H^+]) \qquad (4)$$



SCHEME 1

Equation (5) implies that k_0 (true rate constant for $ArNHO^+H_2$) is given by $k_N K_a^O/K_a^N$, where K_a^O denotes

$$k_0 = k_N K_a^O[H^+]/K_a^N(K_a^N + [H^+]) \qquad (5)$$

the acid-dissociation constant for the *O*-protonated species. Since the concentration of $ArNHO^+H_2$ is not high as detected by the spectroscopic method, it is difficult to estimate the K_a^O value directly. We assumed a value for pK_a^O based on the following considerations.

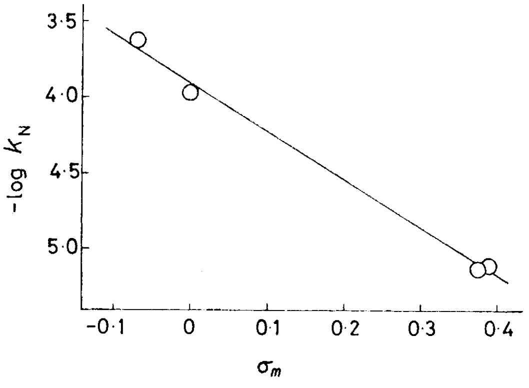


FIGURE 3 Plot of log k_N for the rearrangement of *m*-substituted phenylhydroxylamines against σ_m at 40.0 °C

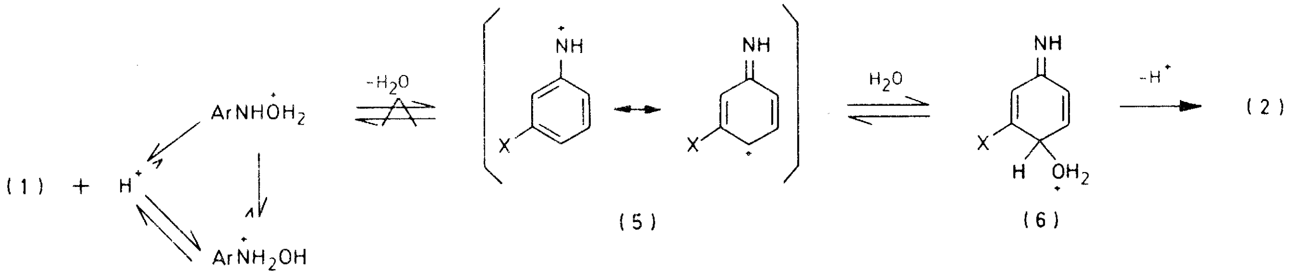
Since the pK_a of ammonium ion (NH_4^+) is 9.24 [11] and that of phenylhydrazinium ion ($PhNHNH_3^+$) is 5.20,[11] the introduction of an anilino-substituent into the ammonium group causes the shift of pK_a by 4.04 units. If the pK_a shift is applied to the oxonium ion (H_3O^+, pK_a −1.74) and $PhNHO^+H_2$, we obtain a pK_a of −5.8 (= −1.74 −4.04) for $PhNHO^+H_2$. Alternatively we can regard $PhNHO^+H_2$ as arising through substitution of the phenyl group of PhO^+H_2 (pK_a −7.0) [12] by the anilino-group: then, since the pK_a difference between anilinium ion ($PhNH_3^+$, pK_a 4.60) [11] and phenylhydrazinium ion ($PhNHNH_3^+$, pK_a 5.20) [11] is 0.60, we can estimate the pK_a of $PhNHO^+H_2$ to be −6.4 (= −7.0 + 0.6). These considerations consistently suggest that the pK_a value of $PhNHO^+H_2$ is *ca.* −6. Hence, K_a^O/K_a^N is *ca.* 10^8.

The Hammett plots of log k_N *versus* σ_m [8] in Figure 3 show a good linear relationship with $r > 0.997$. The ρ value (equivalent to ρ_N) is thus −3.2. Provided that the Hammett rule is valid for all the rate constants and equilibrium constants, equations (6) and (6′) can be

$$\rho_O\sigma_m = \rho_N\sigma_m - \rho_{pK_a^O}\sigma_m + \rho_{pK_a^N}\sigma_m \qquad (6)$$

$$\rho_O = \rho_N + \rho_{pK_a^N} - \rho_{pK_a^O} \qquad (6')$$

derived, where ρ_O denotes the reaction constant for $ArNHO^+H_2$. We have determined ρ_N (−3.2) and $\rho_{pK_a^N}$ (−2.57) but $\rho_{pK_a^O}$ is unknown. We tentatively employed the $\rho_{pK_a^O}$ value determined for the pK_a shift of substituted phenylhydrazines (−1.21).[13] We thus obtained ρ_O −4.6 according to equation (6′). The large negative value means that Bamberger rearrangement by the monoprotonation mechanism is an S_N1-type reaction involving the rate-limiting elimination of water from $ArNHO^+H_2$ to afford the nitrenium ion (5) and the transition state is situated close to (5). If the step (5) ⟶ (6) which corresponds to the nucleophilic attack of water is rate-limiting, ρ_N would have a positive or very small negative value.* The S_N2 mechanism in which elimination of water and nucleophilic attack by water occur simultaneously is also unlikely, because S_N2-type reactions generally feature a much smaller ρ value.



Scheme 2

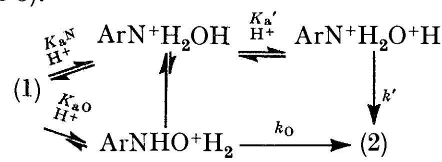
Our conclusion is further supported by the following experimental data. Arrhenius plots for k_N show good linear relationship ($r > 0.998$), and the $\Delta S^‡$ values (Table 2) are all positive. Since the K_a^O/K_a^N value (*ca.* 10^8) is almost constant in the temperature range 20—25 °C, the true $\Delta S^‡$ values estimated for the *O*-protonated species should be much greater. The positive $\Delta S^‡$ values are compatible with the reaction producing two molecules from one. Further important evidence is that the rate constant (k_{obs}) for (1a) in 1N-HCl is identical to that in 1N-H_2SO_4 within experimental error. The products obtained from the reaction in 1N-HCl were 36% *p*-chloroaniline and 64% *p*-aminophenol. Hence, the nucleophilic step [*i.e.* (5) ⟶ (6)] is not involved in the rate-limiting step. The results are consistently rationalized in terms of the S_N1 mechanism and the rate-limiting elimination of water.

Table 2

Activation parameters for k_N

Substrate	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal mol^{-1} K^{-1}
(1a)	24.8	2.4
(1b)	23.8	0.7
(1c)	26.8	3.6
(1d)	26.3	1.9

If the reaction occurred only *via* monoprotonated species (Scheme 2), the plots of k_{obs} *versus* pH (or H_0) would provide a simple saturation profile. We found, however, that the k_{obs} increases further upon decreasing the pH (Figure 3). This finding strongly suggests that, in addition to the monoprotonated species, a diprotonated species has to be taken into account in the H_0 region and that the rate constant for the diprotonated species is much greater than that for the monoprotonated species (Scheme 3).



Scheme 3

The acidity function H_+ for the second proton addition to cationic bases (ArN^+H_2OH) is given by equation (9),

$$H_+ = pK_a' + \log([ArN^+H_2OH]/[ArN^+H_2O^+H_2]) \qquad (9)$$

where K_a' is the acid dissociation constant for $ArN^+H_2O^+H_2$. We tried plots of log k_{obs} in the H_0 region against various H_+ functions,[16] but they did not provide good linearity. It is likely, therefore, that the chemical behaviour of the second proton addition to ArN^+H_2OH is much different from that of conventional second proton addition. We found that the rate constants in the H_0 region can be treated by the linear free energy relationship of Bunnett and Olsen.[17] As shown in Figure 4,

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$$* \quad ArN^+H_2OH \overset{K_1}{\rightleftharpoons} ArNHO^+H_2 \overset{K_2}{\rightleftharpoons} (5) + H_2O \xrightarrow{k_{5\to6}} (6)$$

The rate is given by equation (7) and one can derive equation (7′). Therefore, ρ_N is expressed by equation (8). $\rho_{5\to6}$, $\rho_{pK_a^O}$, and

$$v_{obs} = k_N[ArN^+H_2OH] = k_{5\to6}[(5)][H_2O] \qquad (7)$$

$$= k_{5\to6}K_1K_2[ArN^+H_2OH]$$

$$k_N = k_{5\to6}K_1K_2 = k_{5\to6}K_a^NK_2/K_a^O$$

$$\rho_N = \rho_{5\to6} + \rho_{pK_a^O} - \rho_{pK_a^N} + \rho_{K_3} \qquad (8)$$

ρ_{K_2} are unknown. As described in the text, $\rho_{pK_a^O}$ is *ca.* −1.21. $\rho_{5\to6}$ is the reaction constant for the substituent effect on nucleophilic attack at the *ortho*-position. The value may be approximated by that for nucleophilic substitution of 4-substituted 1-chloro-2-nitrobenzenes by methoxide (+3.90).[14] The ρ_{K_2} is probably greater than ρ_O (−4.6) in equation (6′). The value may also be inferred from the equilibrium between monosubstituted diphenylmethanols and their carbonium ions (−5.24).[15] We therefore presumed ρ_N *ca.* 0. We cannot rule out, however, the possibility that the cited values may be smaller than those in the present reaction. If so, ρ_N could have a positive value.

plots of (log $k_{\text{obs}} + H_0$) against ($\log[H_2SO_4] + H_0$) for (1a—d) provide good linear relationships ($r > 0.998$) in 25—73% sulphuric acid solution where the rates are significantly governed by diprotonated species. On the other hand, the plots deviated from linearity at lower sulphuric acid concentrations where the rates are governed by monoprotonated species. The slopes (*i.e.* ϕ values) were essentially identical (+0.82 ± 0.01), indicating that (1a—d) are subject to the same medium dependence. This means, in other words, that an H_+ function for '*diprotonated species*' does exist and the Bamberger rearrangement involves a diprotonated species as an active intermediate. Okamoto *et al.*[18] inferred, on the basis of analysis of the products from phenylhydroxylamines in acidic solution, that both mono- and di-protonated species may be involved in the Bamberger rearrangement. The present finding is the first, unambiguous evidence for a contribution by a diprotonated species.

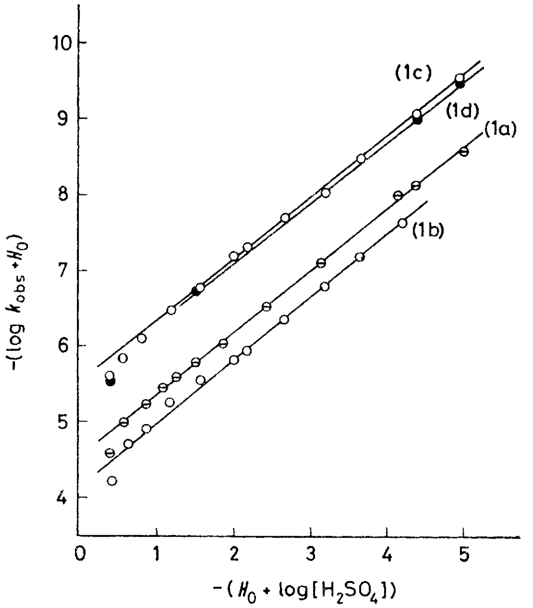

FIGURE 4 Correlation of (log $k_{\text{obs}} + H_0$) for the rearrangement of *m*-substituted phenylhydroxylamines with (H_0 + log $[H_2SO_4]$) at 40.0 °C

Conclusions.—The present study established that (i) the reactive species in the Bamberger rearrangement of phenylhydroxylamines to the corresponding *p*-aminophenols is the mono-*O*-protonated species in the pH region, while both mono- and di-protonated species contribute to the observed reaction rates in the H_0 region and (ii) the rate-limiting step is elimination of water and the reaction is classified as an S_N1 rather than an S_N2 mechanism.

EXPERIMENTAL

Materials.—Phenylhydroxylamine (1a) was prepared from nitrobenzene by zinc powder reduction in aqueous ammonium chloride solution and was recrystallised from benzene–light petroleum, m.p. 81 °C (lit.,[1] 80.5—81 °C), $\lambda_{\text{max.}}$ (1a) 277 nm (ε 950); $\lambda_{\text{max.}}$ (1a)-H$^+$, 268 nm (ε 220). *meta*-Substituted phenylhydroxylamines were prepared from corresponding *meta*-substituted nitrobenzenes by zinc powder reduction in methanolic solution containing ammonium chloride and were recrystallised from benzene–light petroleum: (1b), m.p. 68—69 °C (lit.,[19] 68.5 °C); (1c), m.p. 51—53 °C (lit.,[20] 49 °C); (1d), m.p. 66.0—66.5 °C (lit.,[20] 66 °C); $\lambda_{\text{max.}}$ (ε) (1b), 278 nm (1 010); (1b)-H$^+$, 266 nm (590); (1c), 284 nm (1 180); (1c)-H$^+$, 270 nm (460); (1d), 285 nm (1 290); (1d)-H$^+$, 270 nm (450). *p*-Aminophenol (2a) was purchased from Wako Pure Chemical Co. Ltd., and was recrystallised from water, m.p. 184—185 °C (lit.,[21] 186 °C); $\lambda_{\text{max.}}$ (2a)-H$^+$ 273 nm (ε 1 420). *ortho*-Substituted *p*-aminophenols were prepared according to conventional methods:[22–24] (2b), m.p. 175 °C (lit.,[22] 175 °C); $\lambda_{\text{max.}}$ (2b)-H$^+$ 274 nm (ε 1 670); (2c), m.p. 149—150 °C (lit.,[23] 150—151 °C); (2d), m.p. 163—165 °C (lit.,[24] 165 °C); $\lambda_{\text{max.}}$ (2d)-H$^+$ 279 nm (2 410). Nitrosobenzene (3a) was prepared from (1a) by dichromate oxidation in sulphuric acid solution.[25] m.p. 64—67 °C (lit.,[25] 64—67 °C); $\lambda_{\text{max.}}$ 309 nm (ε 10 000). *meta*-Substituted nitrosobenzenes were prepared from (1b—d) by oxidation in aqueous solution containing iron(III) chloride: (3b), m.p. 53—55 °C (lit.,[19] 53 °C); (3c), m.p. 73—74 °C (lit.,[20] 72 °C); (3d), m.p. 77—78 °C (lit.,[20] 78 °C); $\lambda_{\text{max.}}$ (3b) 313 nm (ε 9 780); $\lambda_{\text{max.}}$ (3c) 306 nm (ε 6 920); $\lambda_{\text{max.}}$ (3d) 307 nm (ε 7 180). Azoxybenzene (4a) was prepared from nitrobenzene in methanolic NaOH,[26] m.p. 36 °C (lit.,[26] 36 °C); $\lambda_{\text{max.}}$ 323 nm (ε 13 000). *m,m'*-Disubstituted azoxybenzenes were prepared from corresponding nitrobenzenes by a similar method: (4b), m.p. 36—37 °C (lit.,[27] 37 °C); (4c), m.p. 96—97 °C (lit.,[28] 96 °C); (4d), m.p. 110—111 °C (lit.,[28] 111 °C); $\lambda_{\text{max.}}$ (4b) 328 nm (ε 12 700); $\lambda_{\text{max.}}$ (4c) 327 nm (ε 13 700); $\lambda_{\text{max.}}$ (4d) 324 nm (ε 14 600).

Spectral and Kinetic Measurements.—U.v. spectra were measured with a Hitachi 323 spectrophotometer equipped with a thermostatted cell-holder. Compound (1) (1.00×10^{-4} mol) was dissolved in water or in aqueous sulphuric acid solution at constant temperature, and spectral scanning from 210 to 360 nm was performed at constant time intervals. Each concentration was determined by extrapolating the time-dependent optical density at $\lambda_{\text{max.}}$ back to zero time.

Kinetic measurements were carried out spectrophotometrically by monitoring the increase of *p*-hydroxyanilinium ion at its absorption maxima. The first-order plots were generally excellent ($r > 0.999$). The molar extinction coefficients of *p*-hydroxyanilinium ions were smaller in the H_0 than in the pH region. It was found, however, that in the H_0 region the rate constants can be determined accurately by the plots since the by-products (3) and (4) were hardly produced in the H_0 region.

The pH values of aqueous sulphuric acid solutions were determined with a Hitachi-Horiba M-7E pH meter. The pH values were shown to be constant during the kinetic measurements. The H_0 values used in this study were taken from ref. 10.

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