M) and varying amounts of a guest were prepared in a cell of either 0.1 or 0.5-cm path length, respectively. The concentrations of guests were so chosen as to meet the Benesi–Hildebrand conditions ($[\text{guest}]_t/[\text{host}]_t > 10$; t = total) and cover a range of 10–90% (mostly 40–80%) complexation. The actual titration data for selected guests are as follows, [guest], mM (θ, mdeg): 20 (0.66), 25 (0.71), 30 (0.77), 40 (0.89), 50 (0.93) for (*S*,*S*)-**2**; 20 (1.19), 30 (1.33), 40 (1.54), 50 (1.63), 67 (1.71) for (*S*)-**8**; 2 (0.46), 4 (0.58), 6 (0.63), 8 (0.66), 10 (0.69), 16 (0.72), 20 (0.73) for **11**; 10 (5.43), 12 (5.90), 15 (6.47), 20 (7.86), 30 (9.29), 40 (10.14) for **14**; 10 (2.18), 12 (2.66), 14 (3.19), 20 (4.20), 25 (5.19), 40 (6.86), 50 (8.43), 80 (11.00). In every case, the Benesi–Hildebrand plots of $[\mathbf{1}]_t l/100\theta$ vs $1/[\text{guest}]_t$ according to eq 2 gave a straight line with r (correlation coefficient) ≥ 0.98. The binding constants and molar elipticities evaluated from the slopes and intercepts are summarized in Table I.[12]

Sugar extraction was performed as described.[5b] Thus, a two-phase mixture of a CCl_4 solution (20 mL) of host **1** (2.0×10^{-4} M) and an aqueous solution (2 mL) of a sugar (5 M for all sugars except for galactose (**22**) and 2.5 M for **22**) was vigorously stirred at room temperature for 24 h. The organic layer was carefully separated,[5b] taken in a cell of a 0.5-cm path length, and subjected to the measurements of CD spectra.

^{1}H NMR Study. The interaction of host **1** (1.0×10^{-2} M) and guest (*R*,*R*)-**2** or racemic **6** in $CDCl_3$ was investigated by means of ^{1}H NMR spectroscopy at 25 °C in exactly the same way with the same machine as described earlier.[7] The complexes **1·2** and **1·6** showed the methyl proton resonances at δ ca. −0.7 and −0.8, respectively. Binding constants of $K_2 = 2.8 \times 10\ M^{-1}$ and $K_6 = 6.7 \times 10\ M^{-1}$ were obtained from the dependence of extents of complexation on guest concentrations: $[\mathbf{1{\cdot}2}]/[\mathbf{1}]_t$ = 0.175, 0.355, 0.430, and 0.601 at $[\mathbf{2}]_t/10^{-2}$ M = 1.0, 2.0, 3.0, and 7.0, respectively; $[\mathbf{1{\cdot}6}]/[\mathbf{1}]_t$ = 0.248, 0.570, 0.640, and 0.698 at $[\mathbf{6}]_t/10^{-2}$ M = 1.0, 2.0, 3.0, and 5.0, respectively. ^{1}H NMR spectra were taken also for a series of solutions under conditions where $[\mathbf{1}]_t + [\mathbf{2}]_t$ was kept constant at 1.0×10^{-2} M. The continuous-variation (Job) plots of $[\mathbf{1{\cdot}2}]$ vs mole fractions of **1** (f) showed a maximum at $f = 0.5$, indicating a 1:1 host:guest stoichiometry; $[\mathbf{1{\cdot}2}]/10^{-4}$ M = 2.7, 3.7, 4.4, 4.8, 4.5, 3.8, and 3.1 at f = 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8, respectively.

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4-[(3,4-Dimethoxyphenyl)azo]pyridine: Two Different Pathways in the Acid Hydrolysis of the Two Methoxy Groups[||,1]

Robin A. Cox,[*,†] Ikenna Onyido,[*,‡] and Erwin Buncel[*,§]

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1, Department of Chemistry, University of Agriculture, Makurdi, Nigeria, and Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6.

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Abstract: The kinetics of hydrolysis of the two methoxy functions in the title compound **1** have been determined as a function of sulfuric acid concentration. Basicity constants for azo group protonation have been evaluated for **1** and several other (phenylazo)pyridines. The 4-OMe group in **1** hydrolyzes very readily in aqueous H_2SO_4 at 25 °C (half-life, seconds to minutes); the 3-OMe group also hydrolyzes, but more slowly (half-life, hours to days). The results extrapolate to a reactivity difference of 7000 in pure water. Both reactions exhibit maxima in the rate constant/percent H_2SO_4 profile. An excess acidity analysis of the rate data reveals that the origins of the deceptively similar rate profiles for the two methoxy functions are different, as are the reaction pathways for the hydrolyses. Hydrolysis of the 4-OMe group occurs via initial activation of the para position through azo protonation, followed by ipso ring carbon attack by three water molecules to give a positively charged intermediate, IH^+. Cleavage of the methoxy C–O bond in IH^+ leads to products. As the three water molecules are active participants in the bond making/breaking processes, either formation or decomposition of the intermediate may be rate-limiting (k_1, k_2 in Scheme I), depending on the log a_{H_2O} values of the medium. For the 3-OMe group, initial azo protonation is in competition with rate-determining ring carbon protonation, which is followed by fast water reaction with the resulting charged intermediate. Azo protonation inhibits the reaction by storing the substrate in an unreactive form, thus accounting for the decreasing reactivity at higher acidities (Figure 1). This is corrected for in the excess acidity treatment, yielding a linear plot (Figure 2). This linear plot is a direct consequence of the lack of requirement for water molecules in the rate-determining step of the 3-OMe hydrolysis. Conversely, the observed rate decrease for the 4-OMe group (Figure 1) results from depletion of the nucleophilic entity (water), which correlates with medium acidity in terms of rapidly diminishing log a_{H_2O} values; this, in turn, manifests in the downward curvature in the excess acidity plot (Figure 2). The totally different mechanisms for the reactions of the 3- and 4-OMe functions unraveled herein provide a framework for discussion of the hydrolyses of unactivated aromatic substrates in acidic media.

Alkyl aryl ethers are generally resistant to hydrolysis in acid media. Conventional cleavage methods include the Zeisel method[2] and treatment with a variety of reagents, such as anhydrous sulfonic acids,[3] Lewis acids,[4] and similar compounds; other methods[5] include phase-transfer catalysis.[6] However, the observations of Witt and Schmidt, published 100 years ago,[7] and kinetic studies by Bunnett and co-workers much later[8] demonstrate

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[†] University of Toronto.

[‡] University of Agriculture.

[§] Queen's University.

[||] This paper is dedicated to Professor Joseph F. Bunnett on the occasion of his 70th birthday.

(1) Mechanistic Studies in Strong Acids. 15. Part 14: ref 20. Heteroaromatic Azo-Activated Substitution. 5. Part 4: ref 10. Studies of Azo and Azoxy Dyestuffs. 21. Part 20: Rajagopal, S.; Buncel, E. *Dyes Pigm.*, in press.

(2) For a general review, see: Bhatt, M. V.; Kulkarni, S. U. *Synthesis* **1983**, 249.

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(4) (a) Guindon, Y.; Yoakim, C.; Morton, H. E. *Tetrahedron Lett.* **1983**, 2969. (b) Johnson, F. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1965; pp 1–109.

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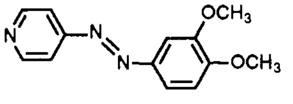
that para phenylazo substitution activates these compounds toward attack by nucleophilic water, provided that the solution is sufficiently acidic to give a reasonable concentration of the protonated substrate. Work in our laboratories in recent years[9-11] has shown that the incorporation of heteroatom centers into the arylazo fragment, particularly when it is done in a way that ensures conjugative interaction between these centers and the reaction site, results in dramatic rate enhancements in the ensuing hydrolysis reactions.[9-11]

The mechanism of these reactions has been discussed in terms of nucleophilic attack on the ipso aromatic carbon,[8,12] and it has been possible to demonstrate base-catalyzed S_NAr reactions of some of these substrates with amine nucleophiles in neutral media such as dimethyl sulfoxide and acetonitrile.[13,14] The present paper reports on a kinetic study of the title compound **1**, in which hydrolysis of the neighboring ether functions occurs consecutively in aqueous sulfuric acid media, extending the available information[8-11] on these processes.



1

The excess acidity method[15,16a] was used to analyze the rate and equilibrium data obtained. This method has been found to be very useful in obtaining mechanistic information concerning a wide variety of reactions which take place in aqueous sulfuric acid media. Examples include amide hydrolysis,[16b] aldol condensation,[18] alkyne hydration,[19] and most recently, aromatic hydrogen exchange;[20] it has been successfully applied previously to phenylazo ether hydrolyses.[9,10] Unexpectedly, in this case it has been found that the two methoxy functions hydrolyze by entirely different mechanisms.

Experimental Section

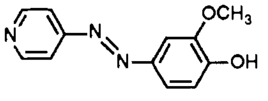
Materials. Sulfuric acid solutions were made up from Fisher Reagent Grade sulfuric acid and freshly distilled water and were standardized by titration. Compound **1** was prepared by the direct coupling of 4-aminopyridine and 1,2-dimethoxybenzene (veratrole) as follows. *tert*-Butyl nitrite (0.02 mol, 2.1 g) was added dropwise with stirring to a solution of 4-aminopyridine (0.02 mol, 1.64 g) in H_3PO_4 (20 mL) at about 0 °C. Dropwise addition of veratrole (0.02 mol, 2.76 g) in MeOH (1 mL) at 0 °C, with vigorous stirring, was followed by neutralization with ice-cold 10% NaOH and extraction with diethyl ether. Distillation of the ether gave a reddish oil, which was dissolved in hot MeOH, poured into cold water, and refrigerated overnight. The resulting yellow solid was recrystallized from 2:5 v/v $MeOH/H_2O$ to give yellow crystals, which were dried under vacuum: mp 71–73 °C, 2.3 g (48%); λ_{max} (MeOH) 373 nm; ^1H NMR ($CDCl_3$) δ 4.03 (6 H, d); 7.05 (1 H, d); 7.54 (1 H, d); 7.70 (2 H, q); 7.73 (1 H, q); 8.80 (2 H, q). Anal. Found: C, 64.15; H, 5.23; N, 17.50. Calcd for $C_{13}H_{13}O_2N_3$: C, 64.17; H, 5.39; N, 17.28. The mono- and dihydrolysis products **2** and **3** were prepared similarly using the appropriate phenols instead of veratrole and were fully characterized spectroscopically.

Basicity Determination. Aliquots (10 μL) of a stock solution of **1** in EtOH (0.003 15 M) were injected into 2 mL of the appropriate acid solution in a 1-cm cuvette. When hydrolysis to **2** was complete (a few minutes) the UV–vis spectra of these solutions were recorded on a Beckmann DU-8 spectrophotometer, with distilled water as a reference. The results given in Table SII of the supplementary material[21] were analyzed as discussed to give the pK_{SH^+}.

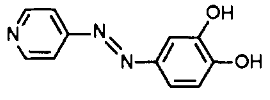
Kinetics. The rate of product formation was monitored spectrophotometrically on either a Beckmann DU-8 or a Perkin-Elmer Lambda 5 spectrophotometer by the direct method for the fast reactions or by the indirect method for the slow reactions, as described previously.[9,22] The 4-OMe reaction was too fast in the 24–44% H_2SO_4 region for convenient measurement by the direct method as described, and it became necessary to initiate the reaction by injecting a concentrated solution of the substrate into the acid solution while stirring. The accuracy of the rate constants obtained using this modification was ensured by standardizing the method with reactions whose rates could be monitored with and without stirring. Rate constants were obtained from plots of ln $(A_\infty - A_t)$ versus time, with excellent linearity being observed in all cases.

Results

Products. Treatment of **1** with aqueous sulfuric acid gives **2** in a fast reaction and then, more slowly, **3**. This was established by spectral comparison of the products with authentic samples of **2** and **3** prepared separately. Product formation was quantitative.



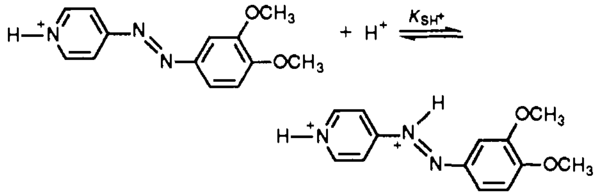
2



3

Basicity. All of the (phenylazo)pyridines with which we have dealt, including **1**–**3**, protonate on the pyridine nitrogen in the pH region,[9] and henceforth it will be assumed that all of the substrates and products are fully protonated on the pyridine nitrogen at the much higher acidities involved here.[9]

A second protonation takes place within the acidity range covered by the kinetic measurements on the azo nitrogen remote from the methoxy substituents,[9] as shown in eq 1. (For ease of handling of subscripts, the equilibrium constant for this second protonation will be referred to as pK_{SH^+}, although strictly speaking it should be $pK_{SH_2{}^{2+}}$.) It was necessary for the kinetic analysis to establish a numerical value for this pK_{SH^+}, but the 4-OMe group of **1** hydrolyzed too rapidly for this to be possible. However, the first reaction product **2** was stable enough to permit equilibrium measurements, and values of Davies–Geissman absorbance differences[23] as a function of acidity for this compound are given in Table SII of the supplementary material.[21,24]



(1)

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(17) A smooth curve with a short plateau in the middle would accommodate all of the points in the upper plot of Figure 3. This would imply that k_1 and k_2 could both be the rate-controlling steps in that region for hydrolysis of the 4-OMe group of **1**. We thank a referee for pointing out this possibility.

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(21) Supplementary material.

(22) (a) Buncel, E.; Lawton, B. T. *Can. J. Chem.* **1965**, *43*, 862. (b) Buncel, E.; Strachan, W. M. J. *Can. J. Chem.* **1970**, *48*, 377. (c) Buncel, E.; Dolenko, A. *Can. J. Chem.* **1974**, *52*, 623. (d) Cox, R. A.; Buncel, E. *J. Am. Chem. Soc.* **1975**, *97*, 1871. (e) Cox, R. A.; Dolenko, A. J.; Buncel, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 471. (f) Buncel, E. *Acc. Chem. Res.* **1975**, *8*, 132.

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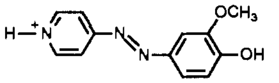
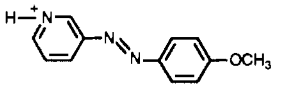
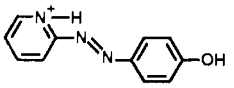
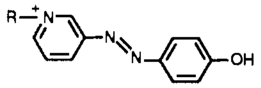
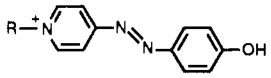
(24) Although the Davis–Geissman method[23] may not account for medium effects on the spectra,[25] taking absorbance differences does remove any variability caused by small concentration differences, etc., and is still preferable to using the absorbances directly.

Table I. Values of pK_{SH^+} and m^* for Some Protonated Phenylazopyridines[a]

compd	structure	pK_{SH^+}	m^*
4[b,c]		−3.66 ± 0.32	0.80 ± 0.10
5[d]		−4.43 ± 0.14	1.49 ± 0.06
6[e]		−4.09 ± 0.26	0.89 ± 0.08
7[e,f]		−3.92 ± 0.14	1.26 ± 0.06
8[e,f]		−2.66 ± 0.24	0.80 ± 0.10

[a] See eq 1. [b] Data from Table SII.[21] [c] $\Delta A_S = -0.402 \pm 0.014$; $\Delta A_{SH^+} = 0.285 \pm 0.023$ (cf. Table SII[21]). [d] Data from ref 9. [e] Data from ref 30a. [f] R = H, CH_3. Both compounds give the same values within experimental error; the ones quoted are weighted averages.

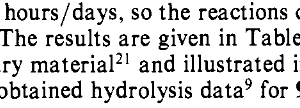
These data were analyzed using the excess acidity method[26] as follows. The basic excess acidity equation is eq 2,[26] where I is the ionization ratio, X the excess acidity, and m^* a slope parameter with values of 1.0 for primary aromatic amines, 0.6 for amides, 1.4 for thio compounds, and so on.[26] The ionization ratio

$$\log I - \log C_{H^+} = m^*X + pK_{SH^+} \qquad (2)$$

$$I = C_{SH^+}/C_S = (\Delta A - \Delta A_S)/(\Delta A_{SH^+} - \Delta A) = \text{antilog}\,(m^*X + pK_{SH^+} + \log C_{H^+}) \qquad (3)$$

is given in terms of the measured absorption differences ΔA by eq 3,[27] where ΔA_S and ΔA_{SH^+} refer to the unprotonated and fully protonated species, respectively; values of the latter are commonly estimated and used with the individual ΔA's to evaluate values of I, which then give pK_{SH^+} and m^* via eq 2. However, it has been found to be more valid statistically to fit the ΔA values directly,[28] using eq 3 with X and $\log C_{H^+}$ as variables, obtaining ΔA_S, ΔA_{SH^+}, and m^* with their standard deviations as coefficients; this was done in this paper using a curve-fitting program modified from Bevington.[29] For comparison, values were obtained for a number of other (phenylazo)pyridines **4–8** as well, using available data;[9,30] all of the results are given in Table I. Medium effects were fortunately absent, but could easily have been accommodated by a slight modification of this procedure.[25]

Kinetics. Rate constants for the successive hydrolyses of both of the methoxy groups of **1** were measured at 25 °C as a function of sulfuric acid concentration. The half-lives are quite different, with that of **1** → **2** being in the seconds/minutes range whereas that of **2** → **3** is hours/days, so the reactions could be followed independently. The results are given in Table SIII and SIV of the supplementary material[21] and illustrated in Figure 1, along with previously obtained hydrolysis data[9] for **9** for comparison.



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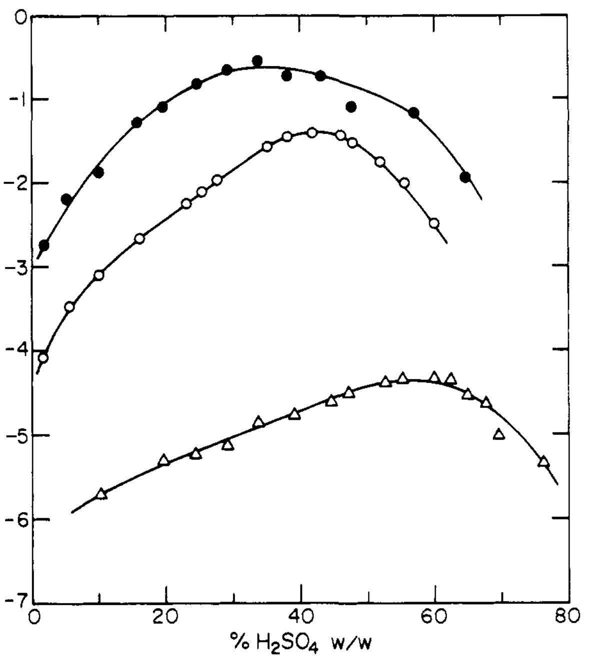

Figure 1. Plots of log k_ψ as a function of percent H_2SO_4 w/w for the hydrolyses of the 4-OMe group of **1** (●) and the 3-OMe group of **2** (△) at 25 °C. Given for comparison is a plot for the hydrolysis of the 4-OMe group of **9** (○).[9]

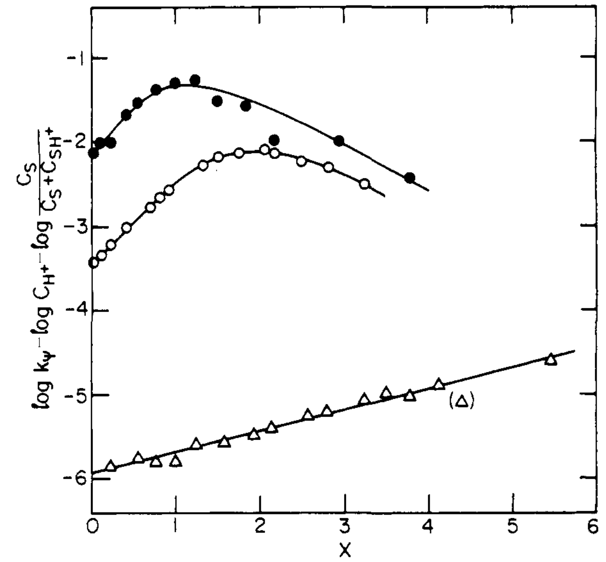

Figure 2. Excess acidity plots for the data of Figure 1, assuming an A-1 or A-S_E2 reaction mechanism. See Figure 1.

The rate data were also analyzed using the excess acidity method.[15,16] To do this, the observed pseudo-first-order rate constants, k_ψ, from Tables SIII and SIV[21] are plotted as $\log k_\psi - \log C_{H^+}$, corrected for substrate protonation, against the excess acidity X.[26] The protonation correction term was $\log (C_S/(C_S + C_{SH^+}))$, i.e., $\log (1/(1 + I))$, which was calculated using eq 3 and the pK_{SH^+} and m^* values for **4** given in Table I. The resulting plots are given in Figure 2, together with one for **9** for comparison.[9] (The protonation correction term for **9** was calculated using the pK_{SH^+} and m^* values for **8** given in Table I.) The top two plots in this figure curve downward at higher acidities, which means that water is involved in an A-2 hydrolysis for the 4-OMe groups in **1** and **9**.[15] However, the bottom plot is linear with a shallow slope, characteristic of an A-S_E2 reaction, which means that hydrolysis of the 3-OMe group of **1** involves rate-determining proton transfer.[15,16a] For this line the slope is 0.253 ± 0.009 and the intercept is −5.950 ± 0.025, with a correlation coefficient r of 0.992; one point was rejected as it was off the line.[20]

Previous work with **9** suggests that the A-2 reaction of the 4-OMe group involves three water molecules.[9] Accordingly, 3

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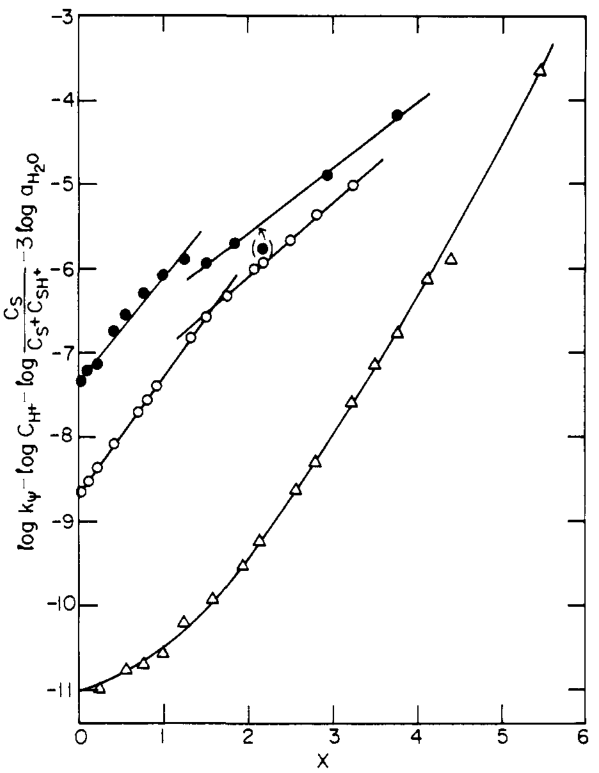


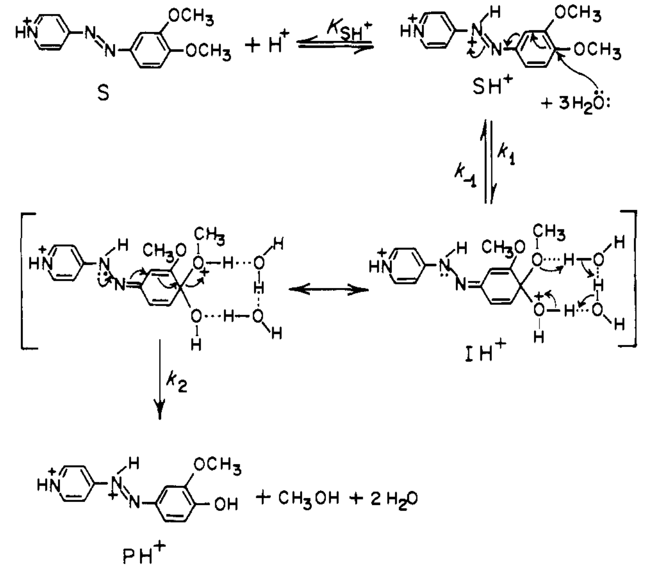
Figure 3. Excess acidity plots for the data of Figure 1, assuming an A-2 reaction with three water molecules. See Figure 1.

log a_{H_2O} was subtracted from the y axis data of Figure 2,[15,31] and the result of this is shown in Figure 3. Now the top two plots are linear but in two parts, whereas the bottom one is necessarily curved. For **9**, which has the better rate data, the first line has slope 1.393 ± 0.006 and intercept −8.699 ± 0.005 (r 0.99994), and the second line has the values 0.872 ± 0.017 and −7.842 ± 0.045 (0.999). Inspection reveals the acidity dependence of the 4-OMe group of **1** to be similar; the values are as follows: first line, 1.248 ± 0.074 and −7.342 ± 0.050 (0.990), and second line, 0.770 ± 0.022 and −7.123 ± 0.058 (0.9992; one point was rejected).

Discussion

Interest in the chemistry of arylazo phenols results from their wide importance as dyestuffs.[33] Our studies of the solvatochromism of pyridinylazo phenols[34] led to the investigation of their methyl ethers as model compounds,[35] and a kinetic study of their acid hydrolysis[9] revealed new mechanistic features compared with their purely aromatic analogues, which had been quantitatively investigated earlier by Bunnett and co-workers.[8] The introduction of two neighboring methoxy functions into these molecules in the present study seeks to ascertain the importance of activation by the protonated azo moiety. This must be at the origin of the greatly increased reactivity of arylazo ethers compared with the aryl alkyl analogues discovered 100 years ago.[7] Since hydrolysis of the 4-OMe group occurs by an essentially acid-catalyzed, activated S_NAr process,[9] would this mechanism persist with the 3-OMe group where such activation cannot readily be envisaged? It will be shown in the ensuing discussion that a detailed kinetic analysis using the excess acidity method[15] has revealed totally different reaction mechanisms for the two stages. While the 4-OMe hydrolyzes by an activated S_NAr process and requires three molecules of water, hydrolysis of the 3-OMe is shown to occur with *ring protonation* as the key step, and there is no water involvement in the rate-determining step. Thus the apparent similarity in the rate profiles in Figure 1 is shown to be illusory. The kinetic analysis which is developed in arriving at these conclusions is preceded by consideration of the equilibrium protonation of the substrate since, clearly, it is the heteroatoms which are of prime importance in determining the unusual reactivity of these molecules.

Scheme I



Basicities. The values of pK_{SH^+} listed in Table I are the thermodynamically correct ones,[26] not the values of H_0 at half-protonation we have discussed before;[9] the two would be the same if the m^* values were 1.0, but they are not, as can be seen from Table I. Compounds **4**, **6**, and **8**, which have nitrogen ortho or para in the pyridine ring, have values of 0.8–0.9 (i.e., these follow a more shallow acidity function than H_0), whereas **5** and **7**, with a meta ring nitrogen, have values of 1.3–1.5 (steeper than H_0). This is a clear reflection of the differing solvation of these ions,[36] probably caused by the higher degree of resonance charge delocalization possible in the ortho or para situation.

Introduction of a second positive charge on the nitrogen next to the ring with the pyridinium substituent (see eq 1) becomes easier as the distance between the positive charge centers increases, as might be expected; thus **6**, **7**, and **8** have pK_{SH^+} values of −4.1, −3.9, and −2.7, respectively. Introduction of a 3-OMe group decreases the pK_{SH^+} by exactly one pK unit (compare **4** and **8**), without changing m^*. This gives some idea of the inductive electron-withdrawing influence of the 3-OMe on the azo nitrogen. Replacing OH by OMe makes only a small difference to the pK_{SH^+} and m^* values, as can be seen from a comparison of **5** and **7**, the only case in which this comparison is possible. This justifies our use of the pK_{SH^+} and m^* values of **4** and **8**, which can be measured, as estimates for those of **1** and **9**, which cannot. Another justification is the linearities found in Figures 2 and 3; if we were using incorrect values, none of these plots should be linear.

Reaction Mechanisms. The proposed mechanism for hydrolysis of the 4-OMe group in **1** (and **9**) is given in Scheme I, which is a consolidation of the previously proposed mechanisms for **9**.[9] First, pyridine-protonated **1** (S in Scheme I) protonates again on the azo group to give SH$^+$ (eq 1 above). This is then attacked by three water molecules at the ipso carbon to give the intermediate IH$^+$, which is resonance-stabilized as shown. The three water molecules must all be involved in bond breaking/making processes at the transition state, since the excess acidity method

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[31] The water activities used are given as mole fractions.[32] For compatibility with the other quantities used, C_{H^+} etc., we have converted these to molarity units, which means that the intercept rate constants, k_1 etc., quoted are true second-order rate constants (i.e., values in 1 M water), rather than values in 55.34 M water.

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separates kinetically-involved water from solvation water[15,16] (which shows up in m^* or $m^\ddagger$).[36] One water molecule is a nucleophile, attacking the ipso carbon, one is an acid, protonating the methoxy oxygen, and the third is an acid/base, transferring protons between the others as shown. Three water molecules were indicated to act in this way before in the hydrolysis of amides in moderately acidic sulfuric acid media.[16b] Since the hydrogen bonds in IH^+ will be collinear, it contains a stable five-membered ring (four oxygens and one carbon); structures of this type have been previously proposed to exist in this medium.[37] Breakup of IH^+ as shown gives the protonated product PH^+.

$$k_\psi(C_S + C_{SH^+}) = k_1 a_{SH^+} a_{H_2O}^3 / f_\ddagger \qquad (4)$$

$$= (k_1/K_{SH^+}) C_S C_{H^+} a_{H_2O}^3 (f_S f_{H^+}/f_\ddagger) \qquad (5)$$

$$\log k_\psi - \log C_{H^+} - \log (C_S/(C_S + C_{SH^+})) - 3 \log a_{H_2O} = \log (k_1/K_{SH^+}) + \log (f_S f_{H^+}/f_\ddagger) \qquad (6)$$

$$\log (f_S f_{H^+}/f_\ddagger) = m^\ddagger \log (f_S f_{H^+}/f_{SH^+}) = m^\ddagger m^* X \qquad (7)$$

If the initial attack by water is rate-determining, the excess acidity kinetic equation that applies can be derived as follows. Using the terminology of Scheme I, absolute rate theory requires that eq 4 holds.[15] Replacement of a_{SH^+} using the definition $K_{SH^+} = a_S a_{H^+}/a_{SH^+}$ and separation of a_S and a_{H^+} into molar concentrations C and activity coefficients f gives eq 5. Rearrangement and taking logarithms gives eq 6, which is linear in X according to eq 7[15,16a] (see Figure 3).

$$k_\psi(C_S + C_{SH^+}) = k_2 a_{IH^+}/f_\ddagger \qquad (8)$$

$$k_1/k_{-1} = a_{IH^+}/a_{SH^+} a_{H_2O}^3 \qquad (9)$$

$$k_\psi(C_S + C_{SH^+}) = (k_1 k_2/K_{SH^+} k_{-1}) C_S C_{H^+} a_{H_2O}^3 (f_S f_{H^+}/f_\ddagger) \qquad (10)$$

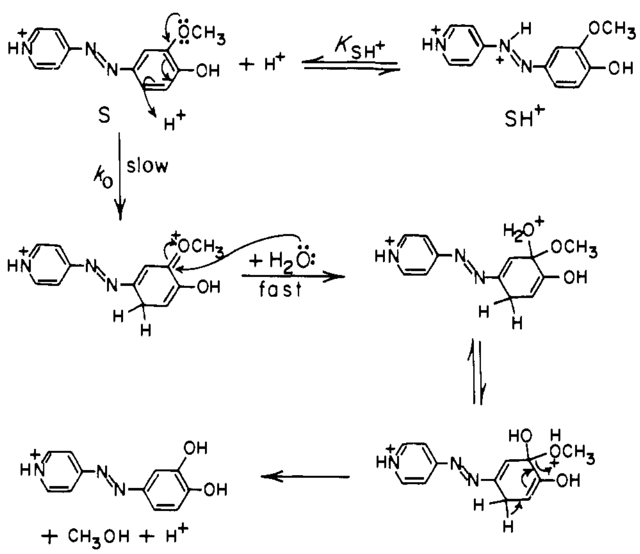
$$\log k_\psi - \log C_{H^+} - \log (C_S/(C_S + C_{SH^+})) - 3 \log a_{H_2O} = \log (k_1 k_2/K_{SH^+} k_{-1}) + m^{\ddagger\prime} m^* X \qquad (11)$$

However, k_1 need not be rate-determining; the breakup of IH^+ (k_2 in Scheme I) could be the slow step. If this is so, eq 8 applies; replacing a_{IH^+} by the equilibrium constant definition of eq 9 leads, after using K_{SH^+} and separating activities as before, to eq 10, which in logarithmic form is again linear in X (eq 11). This equation is of the same form as eq 6, but with a different intercept and a different slope (since the transition states for the two processes are different, $m^\ddagger$ and $m^{\ddagger\prime}$ will not be the same). Thus Figure 3 has two linear regions, the first one having the k_1 step as rate-determining and the second k_2, with a sharp break between them.[17]

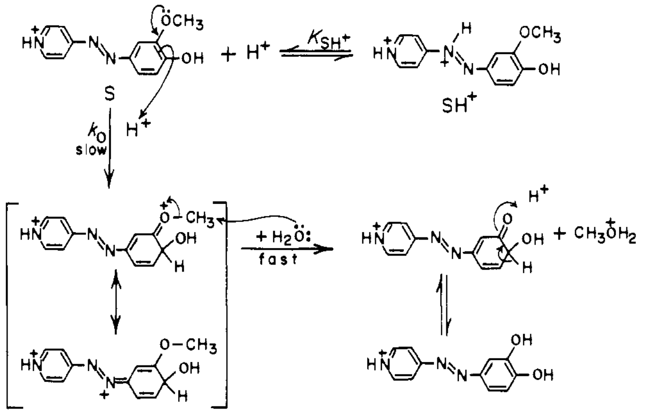
It is quite reasonable to expect the formation of IH^+ to be reversible, since the k_{-1} step to give SH^+ and the k_2 step to give PH^+ are so similar. In fact, the ratio k_2/k_{-1} can be obtained from a comparison of the intercepts of eqs 6 and 11; for **9** this ratio is 7.2 ± 0.7, and for **1** it is 1.7 ± 0.3, in the standard state (water). Entropic considerations alone would slightly favor k_2 in water. Information regarding solvation can be obtained from the magnitudes of the m^* and $m^\ddagger$ slopes;[36] for instance the smaller $m^{\ddagger\prime}$ is associated with the k_2 transition state, so it is more highly solvated than is the k_1 transition state,[36] which again seems reasonable. It follows that the k_2 reaction will be less favored in the more dehydrating stronger acids; hence, the observed switchover of rate-determining steps from the k_1 to the k_2 process.

Whatever the mechanism for the hydrolysis of the 3-OMe group of **1** is, it must be different as is evident from the plots in Figures 2 and 3. Two likely possibilities are given as Schemes II and III, which have precedent in a mechanism originally proposed by Schubert and Quacchia for the hydrolysis of the methoxy group of 3,5-dihydroxyanisole in aqueous perchloric acid.[38] The substrate S still protonates on the azo group to give SH^+, as before, and this must be taken into account. However, the rate-determining step is proposed to be ring carbon protonation; the kinetic behavior found requires a rate-limiting proton transfer.[15] This is a well-known reaction of structurally similar molecules; Kresge's group has extensively investigated the slow carbon protonation of several hydroxy- and alkoxybenzenes in perchloric acid.[39] Subsequent fast steps give the hydrolysis product. The applicable rate equation for both schemes is eq 12, which leads to the predicted behavior of eq 13, as found (see Figure 2).

Scheme II



Scheme III



$$k_\psi(C_S + C_{SH^+}) = k_0 a_S a_{H^+}/f_\ddagger = k_0 C_S C_{H^+} (f_S f_{H^+}/f_\ddagger) \qquad (12)$$

$$\log k_\psi - \log C_{H^+} - \log (C_S/(C_S + C_{SH^+})) = \log k_0 + m^\ddagger m^* X \qquad (13)$$

For an A-S_E2 reaction such as this, the $m^\ddagger$ term has an interpretable physical meaning, being the degree of proton transfer at the transition state.[19,20] To obtain this from the observed combined $m^\ddagger m^*$ of 0.25 we need to know the value of m^*; the value of 0.8 in Table I cannot be used, since this refers to azo group protonation, not ring carbon protonation. Kresge[40] has studied the latter process, however, and values of m^* have been calculated from his data.[26] These are quite variable, ranging from 0.9 to 1.7, and so we can really only say that in Scheme II the k_0 process has an early transition state, with the proton less than half-transferred.

Scheme III shows rate-limiting ring protonation at the para position with respect to the azo moiety, but protonation at either of the ortho carbons as shown in Scheme II is perhaps more likely,

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considering the C–O bond dipole. (Meta protonation is much less probable due to the less favorable resonance interactions.) We have no way of distinguishing these at present, but isotope effect studies may make this possible. Also, Scheme III shows S_N2 attack by water on the methoxy carbon to give the product, whereas Scheme II shows water addition at the ipso carbon as in Scheme I, which has precedent.[38] These two possibilities are in principle distinguishable by ^{18}O-exchange studies; S_N2 attack should not lead to exchange, whereas water addition would.[8] As well, the mechanisms proposed in Schemes II and III could be tested by carrying out an experiment in D_2SO_4/D_2O, which would lead to incorporation of deuterium on the ring but not in the starting material if either of these schemes is correct. Such experiments are under consideration.

Rate comparisons of the two reactions are probably best made in the standard state, water, and the necessary rate constants can be obtained from the intercepts quoted above. In this medium, the 4-OMe hydrolyzes some 7000 times faster than the 3-OMe and by a totally different mechanism.

The foregoing analysis of the rate data clearly shows that, although the gross kinetic features for the hydrolysis of the two methoxy groups in **1**, as demonstrated by the rate constant/percent H_2SO_4 profiles, are similar, their mechanisms of hydrolysis are fundamentally different. Protonation of the azo group activates the 4-OMe toward attack by nucleophilic water (Scheme I). The downturn in rate which is evident in Figure 1 and persists in Figure 2 is a clear manifestation of the depletion of nucleophilic water at higher acidities,[41] reflected in quantitative (thermodynamic) terms by decreasing a_{H_2O}. An interesting feature of this mechanism is the sensitivity of the k_1 and k_2 steps to water availability due to differential demands for solvation. This is a consequence of the involvement of three water molecules in this S_NAr-type reaction, each water molecule being assigned an active role in the bond making/breaking process.

By contrast, the rate-limiting step in the reaction of the 3-OMe group is ring carbon protonation. Since water is involved *after* the slow step of the reaction, the plot in Figure 2 remains linear across the entire range of acidity investigated, once the fraction of the substrate protonated on the azo nitrogen is accounted for. The downturn in the rate of the reaction of the 3-OMe group (Figure 1) is therefore a result of the protonation of the azo nitrogen, which is preferred over carbon protonation on the grounds of basicity, and converts the substrate into an unreactive form. The apparent similarity of the reaction profiles in Figure 1 is hence illusory. Clearly the existence of this totally different mechanism reflects the fact that the 3-OMe is *not* activated by the protonated azo function; however, it does represent a viable pathway for the hydrolysis of such aromatic substrates in moderately concentrated acidic solutions.

The unravelling of these different pathways and the clear demonstration of a dichotomy in the mode of response of the two reacting methoxy functions to increasing acidity both commend the excess acidity method as a diagnostic tool for studying reaction mechanisms in concentrated acid.

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Supplementary Material Available: Tables of absorbance data as a function of acidity for **2** (Table SII) and of rate constants as a function of acidity for the hydrolyses of the 4-OMe group of **1** and the 3-OMe group of **2** (Tables SIII and SIV) (3 pages). Ordering information is given on any current masthead page.

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Chemical Trapping of Electronically Excited Biradicals upon Visible Light-Induced Oxygen-Atom Transfer from NO_2 to Allene and Dimethylacetylene in a Cryogenic Matrix

Munetaka Nakata[†] **and Heinz Frei***

Contribution from the Chemical Biodynamics Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.
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Abstract: Oxygen-atom transfer from NO_2 to allene and dimethylacetylene was observed upon excitation of reactant pairs in solid Ar at wavelengths as long as 585 (NO_2 + allene) and 610 nm (NO_2 + dimethylacetylene). Continuous wave dye laser radiation was used to initiate reaction, and product growth was monitored by FT-infrared spectroscopy. In the case of the allene + NO_2 reaction 2-allyl nitrite radical was obtained as product, while excitation of dimethylacetylene–NO_2 pairs gave acetyl methyl iminoxy radical and dimethylketene + NO. Structures of products were determined by ^{15}N and ^{18}O isotopic substitution and, in the case of allyl nitrite radical, by observation of photodissociation products allene oxide and cyclopropanone. The observed radicals constitute transient biradicals formed upon O-atom transfer that are chemically trapped by NO cage coproduct. Interpretation by aid of literature ab initio results indicates that in the case of allene + NO_2 the observed nitrite radical is 2-allenylidoxy biradical trapped in a B_1 excited state. The iminoxy radical product of the dimethylacetylene photooxidation is a trapped singlet excited acetylmethyl methylene biradical. This is the first insight into O-atom transfer paths involving cumulene and CC triple bonds gained by chemical trapping of excited-state biradicals.

I. Introduction

Knowledge of detailed oxidation paths of small unsaturated hydrocarbons is of strong current interest in the area of product-specific conversion of these abundant chemicals to high-valued compounds.[1] Oxidation mechanisms of unsaturated hydrocarbons are of equal importance in combustion[2] and atmospheric chem-

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Present address: Tokyo University of Agriculture and Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183, Japan.

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