Rearrangement mechanisms for azoxypyridines and azoxypyridine N-oxides in the 100% H_2SO_4 region — The Wallach rearrangement story comes full circle¹

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Abstract: Kinetic studies of the Wallach rearrangements of four azoxypyridines, four azoxypyridine *N*-oxides, and one azoxypyridine *N*-methiodide have been carried out in the 100% H₂SO₄ acidity region. For all of the β -isomers in the study the reactions proceeded at a spectrally measurable rate, and the log observed rate constants were found to be linear functions of the log H₃SO₄⁺ concentration, as previously found for azoxybenzene itself, suggesting that the reaction mechanism for these substrates is the same as that previously deduced for axozybenzene, i.e., a general-acid-catalysis A-S_E2 process. For the α-azoxypyridines no reaction could be observed at all. The two α-azoxypyridine *N*-oxides in the study did react, albeit very slowly, but for these two compounds the log observed rate constants were not linear functions of the log H₃SO₄⁺ concentration, but were instead found to be linear in the H₀ acidity function, which is known for the 100% H₂SO₄ acidity region. It follows that the reaction mechanism for these α-isomers is a different one, presumably an A1 process. This mechanism was proposed back in 1963 for azoxybenzene, but has never actually been observed for any substrate before the work reported in this study. Thus, the Wallach rearrangement story can be said to have come full circle.

Key words: azoxypyridines, azoxypyridine N-oxides, Wallach rearrangement, reactivities, mechanisms.

Résumé : Opérant dans la région d'acidité du H₂SO₄ à 100 %, on a effectué des études cinétiques sur les réarrangements de Wallach de quatre azoxypyridines, de quatre *N*-oxydes d'azoxypyridines et d'un *N*-méthiodure d'azoxypyridine. Pour tous les isomères β de l'étude, les réactions procèdent à des vitesses spectroscopiquement mesurables et on a trouvé que le log des constantes de vitesse observées sont linéaires avec le log de la concentration en H₃SO₄⁺, tel qu'on l'avait observé antérieurement avec l'azoxybenzène lui-même, ce qui suggère que le mécanisme de la réaction pour ces substrats est le même que celui déduit antérieurement pour l'azoxybenzène, c'est-à-dire un processus de catalyse acide générale, A-S_E2. Pour les α -azoxypyridines, on n'a observé aucune réaction. Les deux *N*-oxydes de la α -azoxypyridne réagissent, mais la réaction est toutefois très lente et les log des constantes de vitesses de ces deux produits ne donnent pas de relation linéaire avec le log de la concentration en H₃SO₄⁺; elles sont toutefois linéaires avec une fonction d'acidité *H*₀ qui est connue pour la réaction d'acidité du H₂SO₄ à 100 %. On peut donc en conclure que le mécanisme de la réaction pour les isomères α est différent, probablement un processus A1. Ce mécanisme avait déjà été proposé en 1963 pour l'azoxybenzène, mais il n'avait jamais été observé avec un substrat avant celui rapporté dans ce travail. On peut donc dire que l'histoire du réarrangement de Wallach a retrouvé son point de départ.

Mots-clés : azoxypyridines, N-oxydes d'azoxypyridines, réarrangement de Wallach, réactivités, mécanismes.

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Introduction

Many of the kinetic and other studies of the Wallach rearrangement, discovered in 1880^2 and shown below for azoxybenzene **1**, have been extensively reviewed, along with other aromatic rearrangements.³ Over the years, this reaction has proven to occupy a pivotal position in physical organic chemistry, providing unique insights into reaction mechanisms. For instance, it was the first reaction for which a general-acid-catalysis mechanism in strong aqueous acid media was proved to take place,^{4,5} the possibility having been suggested previously.⁶ Catalysis by the species H_2SO_4 and $H_3SO_4^+$ occurred in concentrated H_2SO_4 , but not by $(H^+)_{aq}$ (or H_3O^+), which was found to be not a strong enough

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Dedicated to the memory of Yvonne Chiang (Mrs. Jerry Kresge), wife, mother, fine chemist.

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acid species to catalyze the reaction.⁴ This was again shown to be the case, quite strikingly, when the reaction was found not to take place at all in HClO₄, a stronger acid than H_2SO_4 in H_0 terms, but containing no acidic species other than $\rm H_3O^+$ and other $\rm (H^+)_{aq}.^7$ Since that time, other general-acid-catalysis mechanisms have been found, for instance, in benzamide hydrolysis,⁸ and others $\rm proposed^8$ in concentrated aqueous acids.



The first kinetic study of the reaction of azoxybenzene,^{9,10} which we reported as early as 1963,⁹ quantified the relationship between substrate protonation ($pK_{BH}^+ = -5.18^{11}$) and rearrangement, and demonstrated the requirement for a second proton transfer;¹⁰ the proposed mechanism involved the formation of a dicationic intermediate, which at the time we wrote as having the structure $2.^{9,10}$ However, recent accurate theoretical calculations on several dicationic intermediates shown to be present in various Wallach rearrangements¹² indicate that the structure is more accurately rendered as 3, with the positive charges being almost entirely situated on the two rings, not on the nitrogens, which retain their lone pairs.¹² Dicationic intermediates can actually be observed as stable species in suitable superacid media.¹³



This prompted the question as to whether a tricationic species, for instance 4, could be generated on going to heteroaromatic structures. (For clarity only one resonance form is given for 3 and for 4.) We have found, using modern theoretical calculations, that the charge distributions in di- (or tri-) cationic intermediates like this can have dramatic effects on their reactivities,¹¹ and we developed a novel method of showing this by using the differences in charge distribution over the two halves of the species concerned.¹¹ The latter study used a series of azoxypyridines and azoxypyridine *N*-oxides. One of the observations that the calculation results helped to explain was the large reactivity difference found between α - and β -isomers of these molecules,^{11,14} and this paper deals in detail with their kinetic behaviour; it happens that as well as the reaction rates being quite different, the reaction mechanisms are different as well. The compounds used in this study, **5–13**, are shown below, in the protonated forms, which are the true reactants,¹¹ the parent species being entirely monoprotonated under the reaction conditions used. (Except for **13**, the counteranions would be sulfate or bisulfate.) The α and β nomenclature is used here in preference to the formal NNO and ONN nomenclature, simply because of the convenience. The pK_{BH}^+ values for diprotonation of those molecules for which these could be measured have been given before.¹¹

Experimental

We have reported the syntheses of **5–12** previously.^{11,15} The methiodide **13** has also been reported;¹⁵ in brief, it was obtained from **6** by methylation, refluxing **6** with a slight excess of methyl iodide for 5 h and recrystallizing the resulting redbrown crystals from ethanol. The acid solutions, in the 100% H_2SO_4 range, were prepared from 96% H_2SO_4 and fuming 30% oleum, and their concentrations determined accurately by conductivity measurements according to Gillespie and Wasif.¹⁶ Reaction rates were determined spectrophotometrically by the "direct method".^{10,11}

The 90%–100% H₂SO₄ acidity region is interesting and not particularly complex, the only species present being H₃O⁺ (there is no free water), HSO₄⁻, H₃SO₄⁺, and undissociated H₂SO₄ molecules.⁴ Accurate H₂SO₄ activities are available,¹⁷ and with these and the value of $(7.8 \pm 1.7) \times 10^{-4}$ mol² l⁻² given by Liler¹⁸ for the best value for the autoprotolysis constant of H₂SO₄ at 25 °C (combined from several sources) it is possible to calculate the concentrations (although not the activities) of the species H₃SO₄⁺ and HSO₄⁻ between 90% and 100% H₂SO₄ (at 25 °C). This was done. Above 100% H₂SO₄ the medium becomes much more complex, as H₂S₂O₇ and higher sulfur acids are formed, together with the ions resulting from their dissociation, and species concentrations cannot be calculated. However, acidity functions for these media are available;¹⁹ the one used in this work is the one generally called H_0 , measured at "room temperature" by Gillespie, Peel, and Robinson.²⁰ This scale was determined using the protonation equilibria of aromatic nitro compounds, which protonate on an oxygen of the nitro group, and was adjudged suitable to use in this work because of the similarity of the nitro compounds to the azoxy compounds used here. (The other acidity scale in these media, measured by Frederick and Poulter²¹ and called H_A, uses protonated uracils and related compounds as indicators and was adjudged to be less suitable.)

All of the observed pseudo-first-order rate constants, k_{ψ} , at different sulfuric acid concentrations, some at 50 °C and some at 65 °C, obtained for **6** and for **8–13** are given as Supplementary data in Tables S1–S7, together with the H_0 values used and the values calculated for the H₃SO₄⁺ concentrations. Rate constants at 25 °C were already available for **1**,^{10,22} and no reaction could be observed for **5** or for **7**.



Results

Previously, we found that the log observed rate constants for **1** were a linear function of the log $H_3SO_4^+$ concentration at sulfuric acid concentrations between 90% and 100%,⁴ and the same was also found to be true, at least under some circumstances, for hexamethylazoxybenzene⁵ and some azoxynaphthalenes.²³ Shown in Fig. 1 are the log rate constants for azoxybenzene **1**^{10,21} plotted against the log $H_3SO_4^+$ concentrations as recalculated for this work; as it can be seen, the linearity is excellent. For these data log rate constant plots against $-H_0$ are known to exhibit multiple curvature.⁴

It therefore seemed reasonable to plot the log rate constant results obtained in this work against the log $H_3SO_4^+$ concentrations in the same way. Dealing with the β -isomers first: Fig. 2 demonstrates the excellent linearity obtained for the azoxypyridines **6** and **8**, and Fig. 3 that obtained for the azoxypyridine *N*-oxide **12** at two temperatures; the results for 10 were very similar. For 10 and 12, results at two temperatures were available; although both temperatures gave linear plots, the slopes were not the same, but we attach little significance to this as the rate data were obtained by two different workers at different times. There could be other reasons. The results for the *N*-methiodide 13 are shown in Fig. 4, which, as might be expected, exhibits very similar behaviour to that of 10. It is shown in Fig. 5 that the observed log rate constants for 10 and 12 are in fact not linear in $-H_0$. The observed slopes, intercepts, etc. for the various correlations in this paper, many of which are shown in Figs. 1–4, are collected together in Table 1.

The α -isomers behaved differently, however; in fact, no reaction at all was observed for the azoxypyridines **5** and **7**. The azoxypyridine *N*-oxides **9** and **11** did react, but much more slowly than did the β -isomers under the same conditions. The log rate constants were not linear in the log

Fig. 1. Plot of log observed rate constants for 1 at 25 $^\circ C$ against the log $H_3SO_4{}^+$ concentration.



Fig. 2. Plot of the log observed rate constants for 6 and 8 at 50 $^{\circ}$ C against the log H₃SO₄⁺ concentration.



Fig. 3. Plot of the log observed rate constants for **12** at 50 °C (lower) and 65 °C (upper) against the log $H_3SO_4^+$ concentration.



Fig. 4. Plot of the log observed rate constants for 13 at 50 $^{\circ}$ C against the log H₃SO₄⁺ concentration.



 $H_3SO_4^+$ concentration, as is illustrated in Fig. 6, however, when the log rate constants for **9** and **11** were instead plotted against the $-H_0$ acidity function for this medium,²⁰ excellent linearity resulted, as can be seen from Fig. 7. The slopes, etc. of these plots are also given in Table 1.

Discussion

The excess acidity (*X*-function) method, developed for the study of the mechanisms of reactions in acid media,¹⁷ has proved itself to be an excellent tool for this task.¹⁷ However,

it does not work well in the 90%–100% H_2SO_4 acidity range, primarily because an extrapolation to pure water is required, which is unrealistic here. It does not work at all above 99.5% H_2SO_4 , as the X-function cannot be defined in this region,¹⁷ and clearly extrapolating to pure water from oleum solutions, which contain no water at all, is not reasonable. Similarly, the Bunnett–Olsen²⁴ and Bunnett²⁵ methods, both of which require the water activity, cannot be used in media, which contain no free water either.

Therefore, in this acidity region it is more reasonable to ascertain whether the log rate constants can achieve linearity

Fig. 5. Plot of the log observed rate constants for **10** and **12** at 50 °C against $-H_0$, illustrating the lack of linearity in these plots for the β -isomers.

when plotted against known species activities or concentrations, or against a reliable acidity function.²⁶ The fact of linearity is what is actually important. The slopes and intercepts of these lines may not mean much, as there is little data with which to compare them, but at least some meaning can be attached to the relative values. As mentioned above, 90%–100% aqueous sulfuric acid is not a particularly complex medium, only four species being present, H_3O^+ , HSO_4^- , $H_3SO_4^+$, and H_2SO_4 , and the concentrations of all of them can be calculated.

Much previous work^{3–5} has led to the conclusion that azoxybenzene itself reacts with undissociated H_2SO_4 molecules in sulfuric acid, which is more dilute than 90%, and with $H_3SO_4^+$ at higher concentrations. The reaction scheme has been given recently¹¹ and need not be repeated here. The linearity against log $C_{H_2SO_4^+}$ also found for all of the β -isomers in this study strongly suggests the same mechanism applies to them. The azoxybenzene mechanism, modified so as to apply to **6**, is given here as Scheme 1; the same Scheme 1 (with suitable atom arrangements) also applies to **8**, **10**, **12**, and **13**.

The α -isomers, however, behave differently; no reaction could be observed at all for **5** and **7**, while for **9** and **11** the log rate constants are not linear functions of log $C_{\text{H}_2\text{SO}_4^+}$, but are instead linear in $-H_0$ (see Figs. 6 and 7). Linearity in different acidity functions has long been attributed to the A1 and A-S_E2 reaction mechanisms;^{17,18,26} this is part of the original Zucker–Hammett hypothesis.²⁷ We have just ruled out an A-S_E2 process for this reaction, leaving an A1 reaction as the only possibility. A likely reaction scheme for this process is given for **9** in Scheme 2. (In Schemes 1 and 2 the proton in dilute acid media is written as having the form H⁺(H₂O)_n, as this is the most likely situation applying there.⁸)

The reaction mechanism shown in Scheme 2 is in fact analogous to one proposed for azoxybenzene 1 itself as far back as 1963,9,10 but never actually observed in practice for any substrate until now. A second protonation of the monoprotonated substrate 9, $pK_{SH}^+ = -10.49$,¹¹ occurs first. Following this, the (third) proton transfer to the azoxy OH group, giving 14, is a pre-equilibrium process, rather than being concerted with water loss and di- (actually tri-) cationic intermediate formation as in Scheme 1, and the actual rate-determining step is loss of water to give the intermediate as shown in Scheme 2. (In Scheme 2, no attempt is made to show the full electron flow from 14 to the intermediate, as this would look confusing.) The actual concentration of the triprotonated precursor must be vanishingly small, even at these acidities, and the formation of the intermediate from it is an uphill process, as we found when we calculated the charge distributions in these species,¹¹ and so the reaction is very slow. Once the intermediate is formed it will react with almost anything nucleophilic very quickly, probably a bisulfate ion at these acidities, as shown. The difference from the β-isomers is that, for these, intermediate formation is downhill in energy,¹¹ and so it can be concerted with the third proton transfer.

The information in Table 1 is useful for internal comparisons of the reactions of 1 and 5-13, but very few other correlations of this type are available for other reactions, and so other comparisons are difficult; for instance, the similar reaction found in the hydrolysis of benzamides at high acidity involves (H⁺)_{aq} as the catalyzing acid, not H₃SO₄^{+.8} We can make no reliable use of the information obtained at different temperatures for two reasons: (i) because the log rate constant data, obtained at 50 °C or at 65 °C, is plotted as functions of H₃SO₄⁺ concentrations calculated at 25 °C (or an acidity function measured at room temperature); and (ii) there is no reliable "acidity" at which to calculate them, since any value will also have variations due to different species concentrations built into it (for instance, we cannot extrapolate to "pure water", as we can when using the excess acidity method¹⁷).

Having said that, there are some conclusions to draw from the information in Table 1. The intercept values for 10 and the corresponding methiodide 13 are about the same, as would be expected. The β -3-isomers react consistently faster than do the β -4-isomers, by about 0.3 of a log unit. The β -4isomers 8 and 12 react at the same rate, whereas the azoxypyridine 6 reacts slightly faster than does the azoxypyridine N-oxide 10. Little difference seems apparent between the axoxypyridines and the azoxypyridine N-oxides. Most of the differences can be explained by considering the charge separation in the various reaction intermediates, and we have already done this.¹¹ Little difference is apparent between the intercepts for the α -isomers 9 and 11. Some comments can be made about the slopes listed in Table 1: it seems that the reaction temperature may have a large effect on them, looking at the differences between the 50 °C and 65 °C results for 10 and 12, but unfortunately, they are in opposite directions for these two; however, the slope for 1 at 25 °C is much smaller than all of the other slopes. The behaviour of the α isomers 9 and 11 seem much the same as one another.



Substrate	$T(^{\circ}C)$	Slope	Intercept	<i>r^a</i>	N^b	$\pm \sigma^c$
Against log $C_{\text{H}_3\text{SO}_4^+}$						
1 (see Fig. 1)	25	0.831±0.013	-2.321±0.018	0.997	25(1)	0.066
5			No reaction			
6 (see Fig. 2)	50	1.755±0.063	-1.521±0.051	0.990	18	0.099
7			No reaction			
8 (see Fig. 2)	50	1.829±0.041	-2.034±0.028	0.995	21	0.091
10	50	1.806±0.035	-1.754±0.019	0.998	13(1)	0.054
10	65	2.44±0.19	-1.413±0.043	0.954	18	0.095
12 (see Fig. 3)	50	1.687±0.057	-2.011±0.044	0.995	10	0.072
12 (see Fig. 3)	65	1.201±0.024	-1.695 ± 0.012	0.995	27(1)	0.041
13 (see Fig. 4)	50	1.515±0.039	-1.697 ± 0.028	0.997	10	0.065
Against –H ₀						
9 (see Fig. 6)	65	2.587±0.070	-35.72±0.83	0.994	18	0.11
11 (See Fig. 6)	65	2.34±0.12	-32.3±1.4	0.986	12	0.12

Table 1. Slopes, intercepts, etc. for the observed log rate correlations for 1, 6, and 8-13.

Note: Errors given are standard deviations.

^aCorrelation coefficient.

^bNumber of points. Any rejected by the program used as being off the line, to 95% confidence, are in parentheses here and in the figures.¹⁷

^cRoot-mean-square deviation between experimental and fitted points.

Fig. 6. Plot of the log observed rate constants for 9 and 11 at 65 °C against the log $H_3SO_4^+$ concentration, illustrating the lack of linearity in these plots for the α -isomers.





-4 -4 -4 -4 -4 -4 -4 -6 -7-7

General conclusions

Having delineated the various possible Wallach rearrangement mechanisms in the 100% H_2SO_4 region, it is of interest that in more dilute acid media another reaction mechanism is possible, proceeding via the monoprotonated species,^{5,23} but only for those azoxy compounds in which the intermediate species can be stabilized in some way. For instance, by the retention of full aromaticity in one of the aromatic rings of several azoxynaphthalenes.²³ If formation of one of these is not possible, the general-acid-catalysis mechanism of **1** is followed,²³ thus completing the spectrum of Wallach rearrangement mechanisms resulting from structural changes, as one traverses the H_2SO_4 acidity region from dilute to moderately concentrated to highly concentrated and oleum media. Moreover, analogies between the Wallach and benzidine rearrangements are apparent,²⁸ such as two possible mechanisms also being possible in this case, involving mono- and di-cationic reaction pathways.²⁹

This whole class of azo and azoxy compounds and the reactions they undergo have contributed much to our understanding of physical organic chemistry. For instance, we have found that there are two different pathways for the Scheme 1.



acid hydrolysis of the two methoxy groups in 4-[(3,4-dimethoxyphenyl)azo]pyridine,³⁰ and an excess acidity analysis of the acid-catalyzed aryl hydroxylation of phenylazopyridines showed that the reaction was an A2 process with nucleophilic attack of HSO_4^- or H_2O on the diprotonated substrate in the slow step.³¹ More generally, studies of the heteroaromatic azoxyarene series led to the examination of the solvatochromic behaviour of hydroxyazo products and their analogs, and the establishment of the π^*_{azo} solvent polarity scale.³² More recently, we have been studying azo moieties as optical transducers, through light absorption, energy transfer, and

cis/trans isomerism, for molecular photo switching.³³ This continues to be a very fruitful area of research.

Supplementary data

Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3970. For more information on obtaining material, refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml.

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