J. Am. Chem. Soc. 1983, 105, 4299-4302

similar fashion from the reaction of $HAuCl_4$ with dimethylglyoxime.[38]

When the initial pH of the reaction is adjusted between 3 and 5, $[Au(terpy)Cl]Cl_2 \cdot 3H_2O$ is obtained in good yield (~75%). The mixed-valent complex **2** is also a byproduct of this reaction (≤5% yield). When the pH of the reaction is initially adjusted to 7 or above, complete reduction to gold metal is observed. Formation of the metal must result from the reduction of $[AuCl_4]^-$ since solutions of $[Au(terpy)Cl]Cl_2$ are stable under these conditions.

The aqueous solution chemistry of $[Au(terpy)Cl]^{2+}$ can be compared to that of the structurally analogous $[Au(dien)Cl]^{2+}$ complex. The reaction between $HAuCl_4$ and dien similarly produces a variety of products as a function of pH.[18] In the low pH range (<2), the tetrachloroaurate salt of dien, $[H_3dien][AuCl_4]$, is produced in a reaction which resembles reaction 1. When the reaction is carried out at pH ~4, the main product is the $[Au(dien)Cl][AuCl_4]_2$ salt. Although the analogous $[Au(terpy)Cl][AuCl_4]_2$ complex has yet to be isolated, it is possible that this product is one of the unidentified materials obtained in small quantities from reaction 1.

Conclusion

The structure of the cation in $[Au(terpy)Cl]Cl_2 \cdot 3H_2O$ is similar to those of the analogous terpyridine complexes of Pd(II) and Pt(II). The planar $[Au(terpy)Cl]^{2+}$ cation contains elongated axial ligand contacts to H_2O and Cl^- in the crystal lattice, however, and does not form a stacked arrangement of planar cations as found in the structures of the related Pd(II) and Pt(II) complexes. The chemistry of $[Au(terpy)Cl]^{2+}$ in water resembles that of the structurally analogous Au(III) complex of diethylenetriamine, $[Au(dien)Cl]^{2+}$. The insoluble mixed-valent Au(III)-Au(I) compound $[Au(terpy)Cl]_2[AuCl_2]_3[AuCl_4]$, which forms as a byproduct of the reaction used to prepare $[Au(terpy)Cl]^{2+}$, is composed of a chain of three linear $[AuCl_2]^-$ anions that link two $[Au(terpy)Cl]^{2+}$ cations through long axial, Au(III)-Au(I), contacts. The $[Au(terpy)Cl]^{2+}$ cations in the mixed-valent salt are further linked together through axial interactions to the chlorine atoms of the square-planar $[AuCl_4]^-$ anion.

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Registry No. 1, 85719-47-7; **2**, 85709-76-8; **3**, 85709-77-9.

Supplementary Material Available: Atomic positional and thermal parameters for compounds **1** and **2** (Tables S1 and S2) as well as final observed and calculated structure factors (Tables S3 and S4) (31 pages). Ordering information is given on any current masthead page.

Studies in Aromatic Nitration. 2.[1] ^{14}N NMR Study of the Nitric Acid/Nitronium Ion Equilibrium in Aqueous Sulfuric Acid

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Abstract: The nitric acid/nitronium ion equilibrium at 25 °C in aqueous sulfuric acid (81-96%) has been studied by ^{14}N NMR spectroscopy. In contrast to observations by Seel et al. (1972), who obtained only one NMR signal, we observed separate signals for nitric acid and nitronium ion. A 50% conversion of added nitric acid into nitronium ion is observed in 88% sulfuric acid, a value in good agreement with that obtained by others using Raman spectroscopy. From the line-shape analysis of these spectra, pseudo-first-order rate constants for the formation and hydration of nitronium ion were obtained. Examination of these data reveals certain inconsistencies between the currently accepted mechanism and observed rates and orders of aromatic nitration.

We present here the results of our investigation of nitric acid/nitronium ion equilibrium using ^{14}N NMR spectroscopy. Our findings reveal inconsistencies between the accepted mechanism and the observed rates and orders of aromatic nitration. The classical studies of Ingold and Co-workers[2] established that nitration of aromatic compounds in nitric acid-sulfuric acid mixtures proceeds through the intermediacy of the nitronium ion (Scheme I), where k_1 and k_{-1} are respectively the pseudo-first-order rate constants for the formation and hydration of nitronium ion and k_r is the specific rate of reaction of the nitronium ion with the aromatic substrate. The formalism used in this paper is that of Moodie, Schofield, and Taylor.[3]

Scheme I

$$HNO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ \tag{1}$$

$$NO_2^+ + ArH \xrightarrow{k_r} \text{products} \tag{2}$$

Nitric acid in an acid-catalyzed step is first reversibly transformed into nitronium ion, which then reacts with the aromatic to form products. Such a scheme leads to the following rate expression for the formation of nitro products:

$$\text{rate} = \frac{k_1 k_r [ArH][HNO_3]}{k_{-1} + k_r[ArH]} \tag{3}$$

An independent determination of the rate constants k_1 and k_{-1} is thus of crucial importance to the mechanism of aromatic nitration.

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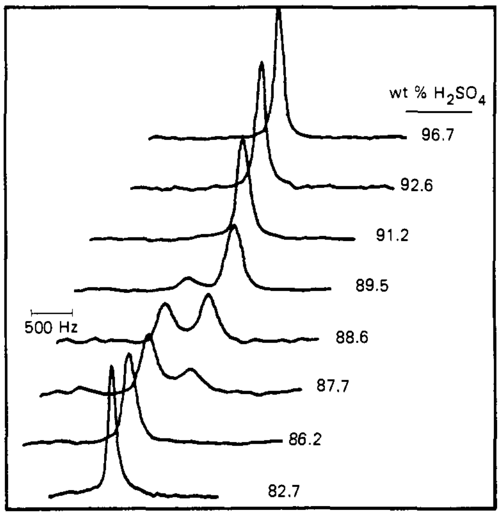

Figure 1. ^{14}N NMR spectra of 0.5 M solutions of HNO_3 in aqueous sulfuric acids; (—) offset between spectra = 220 Hz.

Various spectroscopic techniques, including UV[4] and Raman,[5-7] have been used to study equilibrium 1. Chedin performed an extensive Raman spectroscopic study of the nitric and sulfuric acid systems and obtained the fraction of N(V) species present as NO_2^+ over a range of acidities.[5] Later, Zaman confirmed his observations and extended the study to include temperature dependence of the equilibrium.[6]

Although these studies yield information regarding the relative amounts of nitric acid and nitronium ion, they do not furnish rate data. Bunton studied the exchange of label between nitric acid and ^{18}O-labeled water and determined the rate constant k_1 in aqueous nitric acid.[8] Other attempts at obtaining the estimates of k_1 and k_{-1} have all been indirect.[3,9,10] These studies have involved measuring the kinetics of nitration of aromatic compounds under a variety of conditions and deconvoluting the kinetic data to obtain values for k_1 and k_{-1} on the basis of a presumed mechanism for aromatic nitration.

Results

Recently, Seel et al. examined equilibrium 1 using ^{14}N NMR spectroscopy.[11] They observed that mixtures of pure nitric acid and sulfuric acids give only one broad ^{14}N resonance and that the chemical shift of the signal changed with the ratio of the acids. They concluded from this study that the exchange was fast, although no rate data were presented. Also, the signals for solution with H_2SO_4 greater than 77 mol % were very broad with half-width at half-height around 200 Hz. Seel investigated the nitric acid–nitronium ion equilibrium along the N(V)–H_2SO_4 axis. Nitrations, on the other hand, are generally performed in solutions that are essentially binary in H_2O and H_2SO_4 and to which only a small amount of N(V) is added. We therefore decided to study equilibrium 1 along the H_2O–H_2SO_4 axis using ^{14}N NMR spectroscopy. One potential advantage of such a study would be the direct and independent determination of k_1 and k_{-1}.

Table I. Rate and Equilibrium Data for the HNO_3/NO_2^+ System in Aqueous Sulfuric Acids

% H_2SO_4	$-H_0$[a]	$-\log a_W$	% $[NO_2^+]/[N(V)]$	$\log k_1$ (s^{-1})	$\log k_{-1}$ (s^{-1})
81.0			0		
86.2	8.46	2.96	12	2.26	3.11
87.7	8.68	3.15	34	2.45	2.74
88.6	8.82	3.26	54	2.48	2.41
89.5	8.95	3.36	66	2.59	2.30
91.2	9.21	3.55	92	3.44	2.18
92.6	9.41	3.72	98	3.51	1.91
96.7	10.03		100		

[a] Hammett acidity function.

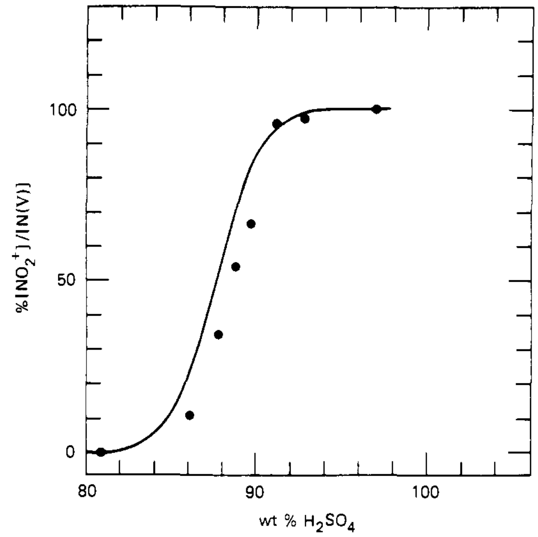

Figure 2. Conversion of HNO_3 into NO_2^+ with % H_2SO_4: (—) Raman spectroscopy study, ref 7; (●) ^{14}N NMR study with HNO_3.

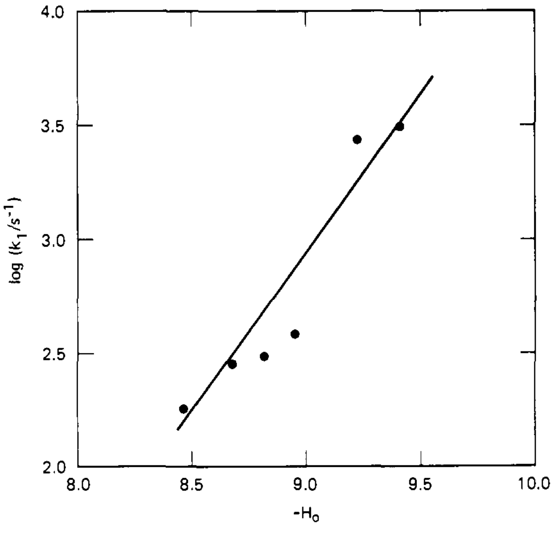

Figure 3. Variation of $\log k_1$ with $-H_0$: $d[\log k_1(s^{-1})]/d(-H_0) = 1.5 \pm 0.2$.

Accordingly, we prepared 0.5 M solutions of HNO_3 in aqueous sulfuric acids of various strengths and obtained their ^{14}N NMR spectra at 25 °C. In contrast to the observations by Seel, these solutions gave separate signals for nitric acid and nitronium ion (Figure 1).[12] In sulfuric acid below 85 wt %, only the signal due to nitric acid could be observed. As the acidity was increased, the intensity of that signal decreased, with the simultaneous appearance of another signal; this one is due to nitronium ion. In

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(12) Ammonium nitrate in aqueous H_2SO_4 (85–100%) displays analogous behavior. Chemical shifts on HNO_3 and NO_2^+ from the central line of the NH_4^+ signal, 316 and 226 ppm, respectively, are in good agreement with Seel's results.

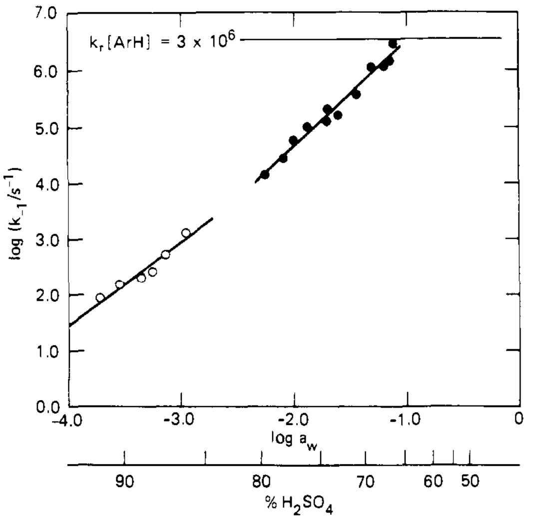

Figure 4. Acidity dependence of the pseudo-first-order rate constant for hydration of nitronium ion (k_{-1}): (●) ref 3, d(log k_{-1})/d(log a_w) = 1.95; (○) this work, d(log k_{-1})/d(log a_w) = 1.51.

solutions of acidities greater than 93% H_2SO_4, the signal due to nitric acid could not be detected.

The resonances in the intermediate range are broad and suggest a chemical exchange. Line-shape analysis of the spectra yielded the relative amounts of nitric acid and nitronium ion, and also the pseudo-first-order rate constants for the formation and hydration of nitronium ion. These results are presented in Table I.

Figure 2 compares our data for the degrees of conversion of nitric acid into nitronium ion over the range of acidities with those from the most recent Raman spectroscopic study.[7] The two studies are in good agreement, and the point of 50% conversion at 25 °C is at about 88% H_2SO_4.

Formation of nitronium ion is an acid-catalyzed process. The pseudo-first-order rate constant for this process, k_1, includes a term that is a measure of the acidity of the medium. The observed first-order rate constant therefore increases with increasing acidity. In Figure 3 log k_1 is plotted against the Hammett acidity function H_0 of the various solutions.[13] The H_0 function is used merely as a convenient acidity scale with no mechanistic implications. The slope of the least-squares line is 1.5 ± 0.2, which is the same as the value obtained by Moodie, Schofield, and Taylor from their nitration studies.[3] Indeed, the two sets of data lie along the same line.

The first-order rate constant for the hydration of nitronium ion, k_{-1}, decreases with increasing acidity. This decrease is expected because k_{-1} is the product of the rate constant for hydration, k_{-1}', and some power of a_w, the activity of water; $k_{-1} = k_{-1}' a_w^n$. The value of n is shown to be about 1.5 from the plot of log k_{-1} vs. log a_w in Figure 4. Moodie et al.[3] had reported an order of 1.95 in water for the same reaction, albeit in somewhat lower acidities. However, there is a reasonably good agreement between the two sets of data.

The NMR signals due to HNO_3 and NO_2^+ in 88.6% H_2SO_4 coalesce upon warming. Figure 5 shows the temperature dependence of the signals from 14.2 to 43.0 °C. Line-shape analyses of these spectra yield the temperature dependence of k_1 and k_{-1}. From the Arrhenius plots, activation parameters were obtained:

$$k_1: \ \Delta H^{\ddagger} = 14.3 \pm 2.6 \text{ kcal/mol}; \ \Delta S^{\ddagger} = 0 \pm 8 \text{ gibbs/mol}$$

$$k_{-1}: \ \Delta H^{\ddagger} = 16.8 \pm 2.4 \text{ kcal/mol}; \ \Delta S^{\ddagger} = 8 \pm 8 \text{ gibbs/mol}$$

The absence of a large negative entropy of activation for the hydration of nitronium ion seems to be inconsistent with a one-step termolecular mechanism (Scheme II) proposed by Moodie et al.[3]

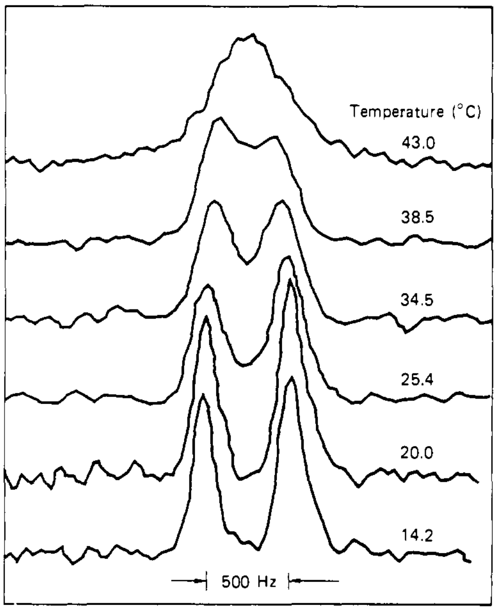

Figure 5. Temperature dependence of ^{14}N NMR of 0.5 M HNO_3 in 88.6% H_2SO_4.

Scheme II

$$NO_2^+ + H_2O + B \rightleftharpoons BH^+ + HNO_3$$

and also for the two-step mechanism shown in Scheme III in which step b is rate limiting. However, compensative entropy changes associated with the solvent reorganization could well be large and preclude any definitive conclusion. Thus, on the basis of the present study it is not possible to differentiate between Schemes II and III. We expect to report on this aspect in greater detail in a subsequent paper.

Scheme III

$$NO_2^+ + H_2O \overset{a}{\rightleftharpoons} H_2NO_3^+$$

$$H_2NO_3^+ + B \overset{b}{\rightleftharpoons} HNO_3 + BH^+$$

Discussion

The close agreement between the rate data for the formation and hydration of nitronium ion as derived from nitration studies by Moodie and co-workers[3] and the rate data obtained by direct NMR measurements suggests that we have provided further evidence for the nitronium ion mechanism for aromatic nitrations. However, as we will demonstrate in this section, both equilibrium and rate data reveal inconsistencies in the mechanism of aromatic nitration.

Equilibrium Considerations. Profiles of observed second-order rate constants of nitration of various aromatic substrates show maxima around 90% H_2SO_4.[13] Vinnik et al.[15,16] showed that, in these strongly acidic media, effects of the media come into play, and if the observed rate constant is corrected by dividing it by the activity coefficient of the aromatic substrate, the profile then exhibits no maximum. The corrected second-order rate constant thus increases steadily with increasing acidity until it finally levels off at a limiting value.

This behavior is easily understood in terms of the nitronium ion mechanism. The increase in the fractional conversion of nitric acid into nitronium ion with increasing acidity results in the increased observed second-order rate constant. But the match

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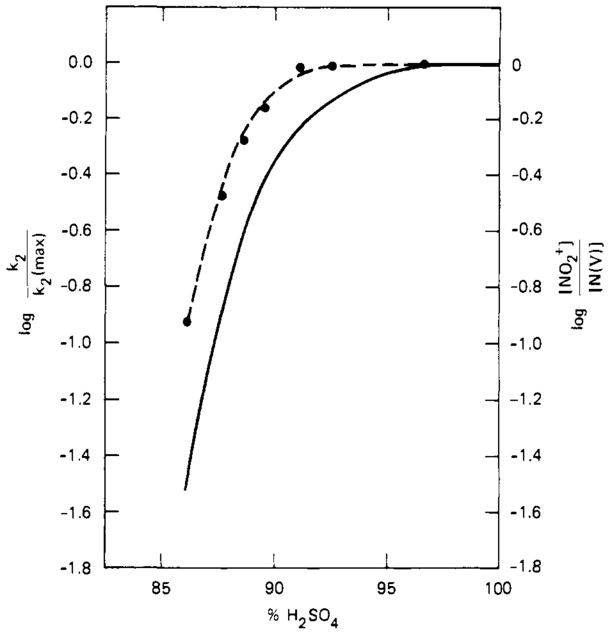

Figure 6. Comparison of the rate profile for nitration of *p*-nitrotoluene and conversion of nitric acid into nitronium ion: (—) log $[k_2/k_2(\max)]$, ref 15; (●) log $\{[NO_2^+]/[N(V)]\}$.

is less than perfect. Figure 6 compares the profile of the corrected second-order rate constant for the nitration of *p*-nitrotoluene[15] with the fractional conversion of nitric acid into nitronium ion. As can be seen, the conversion of nitric acid into nitronium ion reaches a limiting value at lower acidities than the rate constant for nitration. Thus in going from 90% to 95% H_2SO_4, the nitronium ion increases in concentration by about 20% whereas the corresponding nitration rate increases by a factor of 2.3.

Kinetic Considerations. The rate expression for the nitration reaction proceeding according to Scheme I is given by eq 3. Under most conditions of nitrations, k_{-1} is considerably larger than $k_r[\mathrm{ArH}]$ and the rate expression simplifies to eq 4 which explains

$$\text{rate} = \frac{k_1 k_r [\mathrm{HNO_3}][\mathrm{ArH}]}{k_{-1}} \qquad (4)$$

the commonly observed first-order dependence in ArH. When $k_{-1} \sim k_r[\mathrm{ArH}]$, a departure from this behavior is expected, and when k_{-1} is substantially less than $k_r[\mathrm{ArH}]$, the nitration process should be zero order in aromatic.

$$\text{rate} = k_1[\mathrm{HNO_3}] \qquad (5)$$

Indeed, such zero-order behavior in aqueous sulfuric acid has been sought by many investigators but not found, although a departure from strict first-order behavior has been observed.[3] Lack of zero-order dependence of ArH for even such reactive aromatics as anisole ($k_r = 6 \times 10^8$ M^{-1} s^{-1}) at concentrations of 5×10^{-3} M is inconsistent with the values of k_{-1} as projected by our study and also with those in the literature.[3] Also presented in Figure 5 are the values of log k_{-1} calculated from the work of Moodie et al.[17] The two sets of data span different regions of acidity, but agreement between them can be inferred by the fact that a smooth curve could adequately fit both sets of data. From Figure 5 it is seen that $k_{-1} = 3 \times 10^6$ s^{-1} for about 65% H_2SO_4. At 72% H_2SO_4, k_{-1} is 3×10^5 s^{-1}, a value considerably less than $k_r[\mathrm{ArH}] \sim 3 \times 10^6$ s^{-1}. Under these conditions, if Scheme I were operative, zero-order nitration in anisole should have been observed.

Given k_{-1} and the fact that zero order in aromatic was not observed, we can estimate an upper limit for the value of k_r at any given acidity. In 80% H_2SO_4, with [anisole] = 9.9×10^{-3} M, we find that $k_r \leq 1.3 \times 10^6$ M^{-1} s^{-1}, or at least two orders of magnitude less than the expected bimolecular rate coefficient for encounter between two species in this medium. This discrepancy raises a serious question about the validity of Scheme I on the basis of the hypothesis of encounter rate control for the nitration of anisole. It should be pointed out that including an extra step (encounter pair formation or electron transfer) does not resolve the discrepancy. We suggest that a reinvestigation of the kinetics of mechanism of aromatic nitrations is in order.

Experimental Section

Stock sulfuric acid solutions were prepared by diluting reagent grade sulfuric acid (98.6 wt %). The acidity of each of these diluted acids was determined by alkalimetry with a Metrohm Potentiograph Model E436 titrator. HNO_3 (100%) was obtained by distillation from oleum under reduced pressure and was kept frozen until just before use. The NMR tubes were sealed under vacuum and stored in a dry ice/acetone bath. The ^{14}N NMR spectra were recorded on a Varian Model FT 80A instrument equipped with an external ^{2}H lock and a temperature controller. Generally 25 000 transients were accumulated with pulse widths of 30 μs and an acquisition time of 10 ms. Acoustic ringing in the probe caused an undulating base line. For line-shape analyses, the program was modified to include a quadratic and a linear term for the base line. This treatment adequately corrected the base line. The reported percent H_2SO_4 of each solution is the titrimetric value that has been corrected for the formation of water and consumption of H_2SO_4 according to eq 6. The Hammett acidities are those due to Ryabova et al.[18] The

$$\mathrm{H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_2O + H_2SO_4} \qquad (6)$$

activity of water data were obtained by interpolation of data given in the International Critical Tables.[19]

Acknowledgment. Support for this work under United States Army Research Office Contract No. DAAG29-80-C-0046 is gratefully acknowledged. We acknowledge very helpful discussions with Professor Roy Moodie and we also wish to thank Dr. J. Shoolery of Varian Associates, Palo Alto, for his help in recording the NMR spectra.

Registry No. Nitric acid, 7697-37-2; nitronium ion, 14522-82-8.

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