

## Kinetics and Mechanisms of the Oxidation of Hydroxylamine by Aqueous Iodine

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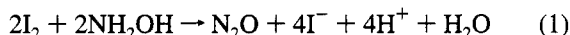
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First-order rate constants ( $k_r$ , 25.0 °C,  $\mu = 0.50$  M) for the loss of  $I_3^-/I_2$  in the presence of excess  $NH_3OH^+/NH_2OH$  are measured from pH 2.0 to 6.8 with variation of the reactant concentrations as well as the concentrations of  $I^-$  and various buffers. The  $k_r$  values range from  $5 \times 10^{-4}$  to  $2 \times 10^4$  s $^{-1}$  and depend on the  $NH_2OH$  concentration. A multistep mechanism is proposed where  $I_2$  and  $NH_2OH$  react rapidly to form an  $I_2NH_2OH$  adduct ( $K_A = 480$  M $^{-1}$ ) that undergoes general-base (B) assisted deprotonation to give  $INHOH + I^- + BH^+$ . At higher pH, hydroxylamine acts as a general base as well as a reductant. Rate constants for various bases ( $H_2O$ ,  $CH_3COO^-$ ,  $NH_2OH$ ,  $HPO_4^{2-}$ , and  $OH^-$ ) fit a Brønsted  $\beta$  value of 0.58. The rates decrease greatly with increases of  $H^+$  and  $I^-$  concentrations due to  $NH_3OH^+$  and  $I_3^-$  formation, loss of general-base assistance, and the reverse reaction of  $BH^+ + I^- + INHOH$  to re-form  $I_2NH_2OH$ . The  $INHOH$  species is a steady-state intermediate that decays to form  $I^- + HNO + H^+$ . Subsequent rapid dehydrative dimerization of  $HNO$  gives  $N_2O$  as the final product. The hydroxylamine oxidation process proceeds entirely by  $I^+$  transfer to nitrogen followed by  $I^-$  loss, as opposed to electron-transfer pathways. Kinetic evidence is given for  $I_2NH_2OH$  as an intermediate and for  $INHOH$  as a steady-state species.

## Introduction

Hydroxylamine is used synthetically to form oxime derivatives that are important in the production of pharmaceuticals and polymers. It is also widely used as a reducing agent for photographic processes, dyeing, and other industrial applications.<sup>1,2</sup> In many reactions of hydroxylamine with oxidizing agents the  $NH_2O^*$  radical is postulated as an intermediate that can decompose to  $N_2$  or be further oxidized to  $N_2O$ . Most of these reactions are with one-electron oxidants.<sup>3</sup> Halogens are two-electron oxidants that react very rapidly with  $NH_2OH$ , as shown in recent kinetic studies with chlorine<sup>4</sup> and with bromine.<sup>5</sup> We now compare the reactivity and reaction mechanisms of iodine with the other halogens. We also address the question of whether these oxidations proceed by electron-transfer steps or by halogen cation transfer followed by halide ion elimination.

In the presence of excess hydroxylamine, iodine is rapidly reduced to iodide ion and hydroxylamine is oxidized to nitrous oxide (eq 1). This stoichiometry has been shown to be valid

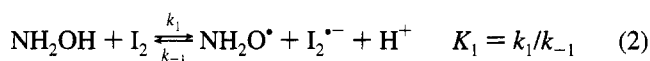


in weakly basic medium<sup>6</sup> as well as in acidic solutions.<sup>7</sup> Although nitrous acid (HONO) can form in acidic solutions when iodine concentrations exceed the total hydroxylamine concentration, no traces of HONO were found when hydroxylamine was in excess from pH 3.4 to 5.5;  $N_2O$  was the only nitrogen product.<sup>8</sup>

The kinetics and mechanisms of the iodine oxidation of hydroxylamine were studied in 1982 by Rábai and Beck,<sup>7</sup> in 1987 by Radhakrishnamurti et al.,<sup>9</sup> and in 1992 by Wang et

al.<sup>8</sup> These reports agree that unprotonated hydroxylamine is far more reactive than the protonated species ( $NH_3OH^+$ ) and that  $I_2$  is much more reactive than triiodide ion,  $I_3^-$ . However, these studies disagree with regard to both the magnitude of the rate constants and the mechanisms. Radhakrishnamurti et al.<sup>9</sup> give an impossibly large rate constant of  $3.5 \times 10^{11}$  M $^{-1}$  s $^{-1}$  for the reaction between  $HOI$  and  $NH_2OH$ . This value is impossible because it is 50 times greater than the diffusion-controlled rate constant ( $\sim 7 \times 10^9$  M $^{-1}$  s $^{-1}$ ).<sup>10</sup> These authors also suggest an unreasonably small value of  $0.4$  M $^{-1}$  s $^{-1}$  as the rate constant for the reaction between  $I_2$  and  $NH_2OH$  to form an adduct. Iodine reacts extremely rapidly with  $I^-$  ( $5.6 \times 10^9$  M $^{-1}$  s $^{-1}$ )<sup>11</sup> to form  $I_3^-$  and with  $S_2O_3^{2-}$  ( $7.8 \times 10^9$  M $^{-1}$  s $^{-1}$ )<sup>12</sup> to form the  $I_2S_2O_3^{2-}$  adduct. Hence, the corresponding adduct formation between  $I_2$  and  $NH_2OH$  cannot be 10 orders of magnitude slower. Finally, they<sup>9</sup> indicate a tendency for the iodine and hydroxylamine reaction to reach a limiting rate at high concentrations of hydroxylamine. Wang et al.<sup>8</sup> show that the  $I_2 + NH_2OH$  reaction is much faster, and they find no evidence for a limiting rate up to pH 5.0 with 0.03 M total hydroxylamine ( $[NH_2OH]_T = [NH_3OH^+] + [NH_2OH]$ ).

Radhakrishnamurti et al.<sup>9</sup> suggested an inner-complex mechanism of electron transfer with a pre-equilibrium 1:1  $\sigma$ -CT interaction between  $I_2$  and  $NH_2OH$ . Rábai and Beck<sup>7</sup> suggested  $NH_2OHI^+$  and  $NH_3OHI^{2+}$  as reactive intermediates. Wang et al.<sup>8</sup> suggested both a molecular path with  $NH_2OI_2^-$  as an intermediate and an electron-transfer path (eq 2), where  $k_1 =$



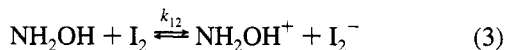
$6.5 \times 10^5$  M $^{-1}$  s $^{-1}$ . We can rule out this electron-transfer

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pathway on the basis of the extraordinarily low self-exchange rate constant for the  $\text{NH}_2\text{OH}^+/\text{NH}_2\text{OH}$  couple, where  $k_{11} = 5 \times 10^{-13} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>13</sup> The  $E^\circ$  value for the  $\text{NH}_2\text{OH}^+/\text{NH}_2\text{OH}$  couple is 0.42 V,<sup>13</sup> the  $\text{p}K_a$  for  $\text{NH}_2\text{OH}^+$  is 4.2,<sup>14</sup> and the  $E^\circ$  value for the  $\text{I}_2/\text{I}^-$  couple is 0.21 V,<sup>14</sup> so the equilibrium constant ( $K_{12}$ ) for the reaction in eq 3 is  $2.8 \times 10^{-4}$ . A self-



exchange rate constant for the  $\text{I}_2/\text{I}_2^-$  couple,  $k_{22} = 8.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ , was estimated in this laboratory,<sup>15</sup> and subsequent work<sup>16</sup> agreed with this value. A recent value of  $k_{22} = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  has been reported.<sup>17</sup> On the basis of Marcus theory,<sup>18</sup> where  $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$  and  $\ln f_{12} = \ln(K_{12})^{2/4} \ln(k_{11}k_{22}/Z^2)$ , the value of  $k_{12}$  is calculated to be  $2.1 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  or less. The value suggested by Wang et al.<sup>8</sup> in eq 2 is more than 10 orders of magnitude larger and is clearly too large to permit an electron-transfer mechanism.

In the present work we examine the kinetics of the  $\text{I}_2/\text{I}_3^-$  reaction with  $\text{NH}_2\text{OH}/\text{NH}_3\text{OH}^+$  over a pH range (2.0–6.8) wider than was previously used, and we test the effects of buffer and reactant concentrations.

## Experimental Section

**Reagents.** Distilled, deionized water was used for all solutions. Ionic strength ( $\mu$ ) was adjusted to 0.50 M with recrystallized  $\text{NaClO}_4$ . Acidity was adjusted with standardized  $\text{HClO}_4$  solutions. An Orion Model SA 720 research digital pH meter and a Corning combination electrode were used to measure pH values which were corrected to  $\text{p}[\text{H}^+]$  values at 25.0 °C and  $\mu = 0.50 \text{ M}$  based on electrode calibration by titration of standardized  $\text{HClO}_4$  and  $\text{NaOH}$ . All chemicals were reagent grade. The concentrations given for kinetic reactions are postmixing values.

Stock solutions of 0.10 M  $[\text{I}_2]_T$  were prepared by dissolving crystalline  $\text{I}_2$  in 0.48 M  $\text{KI}$  solutions. Stock solutions of 0.200 M  $\text{NaI}$  were prepared from the crystalline solid and purged with Ar to remove dissolved  $\text{O}_2$ . These solutions were stored in the dark. Solutions of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (Mallinckrodt) were standardized with  $\text{Fe}_2(\text{SO}_4)_3$ , as previously described.<sup>5</sup> Stock solutions of acetic acid (2.0 M) were prepared from dilution of glacial acetic acid, and buffer solutions were prepared by the addition of 1.0 M  $\text{NaOH}$ . Stock solutions of 0.50 M  $\text{NaH}_2\text{PO}_4$  were prepared from the crystalline salt, and buffer solutions were made by the addition of 1.0 M  $\text{NaOH}$ .

The Griess–Ilosvay reaction<sup>7,19,20</sup> was used to test for nitrous acid by reaction with sulfanilic acid followed by a coupling reaction with 1-naphthylamine to give an azo dye ( $\lambda_{\text{max}} = 520 \text{ nm}$ ). A 1% sulfanilic acid solution was prepared by dissolution of the powder in 25% acetic acid. A 0.6% solution of 1-naphthylamine was also prepared in 25% acetic acid.

**Negative Tests for  $\text{HONO}/\text{NO}_2^-$  as Products.** Since HONO formation and decay was observed in the reactions of  $\text{Cl}_2$  and of  $\text{Br}_2$  with  $\text{NH}_2\text{OH}$ ,<sup>4,5</sup> we tested the stoichiometry given in eq 1 to see if any HONO or  $\text{NO}_2^-$  formed as a byproduct. At  $\text{p}[\text{H}^+] = 6.1$  with 20 mM  $[\text{NH}_2\text{OH}]_T$ , 10 mM  $[\text{I}^-]$ , and  $2.0 \times 10^{-5} \text{ M}$   $[\text{I}_2]_T$ , we found no trace ( $< 10^{-7} \text{ M}$ ) of  $\text{NO}_2^-$  after the reaction with iodine. The Griess–Ilosvay reaction was used. Under the same conditions without  $[\text{I}_2]_T$ , a  $8.4 \times 10^{-6} \text{ M}$   $\text{NaNO}_2$  solution gave an absorbance of 0.289 at 520 nm in a

1 cm cell. At pH 6.1 the reaction between  $\text{NH}_3\text{OH}^+$  and HONO is very slow, as is the reaction between  $\text{I}^-$  and HONO. Hence, we are confident that HONO does not form at this pH.

Reaction products of  $[\text{I}_2]_T$ ,  $[\text{I}^-]$ , and  $[\text{NH}_2\text{OH}]_T$  mixtures were also tested at pH 2–4 and failed to show any evidence of HONO formation. However, at lower pH a proposed<sup>7</sup>  $\text{I}^-$  catalysis of the reaction between HONO and  $\text{NH}_2\text{OH}$  to give  $\text{N}_2\text{O}$  could interfere. We can only conclude that if any HONO had formed, it reacted further to give  $\text{N}_2\text{O}$  and that the overall stoichiometry in eq 1 appears to be valid.

**Kinetic Measurements.** All reactions were followed by the loss of  $\text{I}_3^-$  absorbance at 353 nm ( $\epsilon_{\text{I}_3^-} = 26,400 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>21</sup> in the presence of excess  $\text{I}^-$  and excess total hydroxylamine. Excellent pseudo-first-order rates were observed in accord with eq 4, where  $[\text{I}_2]_T = [\text{I}_3^-] + [\text{I}_2]$  and  $k_r$  is a function of the concentrations of  $[\text{NH}_2\text{OH}]_T$ ,  $[\text{I}^-]$ ,  $[\text{H}^+]$ , and buffer concentrations.

$$-d[\text{I}_2]_T/dt = k_r[\text{I}_2]_T \quad (4)$$

Slower reactions at low pH (half-lives of 36 s to 36 min) were measured with a Perkin-Elmer Lambda-9 UV/vis/near-IR spectrophotometer interfaced to a Zenith 386/20 computer. Reactions in acetic acid/acetate buffer with half-lives of 3 ms to 1 s were monitored by stopped-flow methods by using computer interfaced Durrum or Hi-Tech instruments.<sup>5</sup> Faster reactions (above pH 5) with  $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}$  or  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  as buffers were measured by pulsed-accelerated-flow (PAF) methods.<sup>22–26</sup> Solutions for all PAF experiments were filtered and degassed.

**PAF Method with Integrating Observation.** The PAF Model IV spectrophotometer<sup>24,25</sup> and previous PAF instruments have used integrating observation during continuous accelerated flow mixing of short duration. The light path is along the direction of flow. The measured rate constant depends on the initial absorbance of the reactants,  $A_0$ , the absorbance at a given instantaneous velocity,  $A_v$ , and the final absorbance,  $A_\infty$ . Pseudo-first-order rate constants,  $k_r$ , can be determined by using eq 5, where  $b$  is the reaction path length (0.010 25 m),  $v$  is

$$M_{\text{exptl}} = \frac{A_v - A_\infty}{A_0 - A_\infty} = \frac{1}{bk_m} + \frac{v}{bk_r} \quad (5)$$

the solution velocity (12 to 3 m/s), and  $k_m$  is a proportionality constant from the mixing rate constant ( $k_{\text{mix}} = k_mv$ ). In the PAF integrating observation technique, the reactants are observed from the point where they initially mix until they exit the observation tube. The method is capable of measuring fast reactions with half-lives in the range of 4  $\mu\text{s}$  to 1 ms. However, this PAF method requires knowledge of  $A_0$ . An extremely fast reaction that decreases  $A_0$  prior to the reaction under study will give observed  $k_r$  values that are too large. This problem can be overcome by use of the PAF–PRO instrument in which observation is made across the flow rather than by integrated observation along the direction of flow.

**Pulsed-Accelerated Flow with Position-Resolved Observation.** A new pulsed-accelerated-flow spectrometer with position-resolved observation (PAF–PRO) has been developed in this laboratory.<sup>26</sup> The instrument utilizes a wider range of velocities than the PAF–IV instrument, and observation is perpendicular to solution flow at multiple points in the observation tube. A masked charge-coupled device (CCD) with  $1024 \times 1024$  resolution elements in an  $8 \times 8$  binning mode enables observation at 128 discrete positions along the observation tube (1.945 cm in length). The progress of the reaction is monitored as a function of the distance the solution travels down the observation tube at 126

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different flow velocities in the range of 19.7 to 2.2 m/s. Data for a single kinetic run are collected in 0.5 s with the consumption of 11.0 mL of each reagent. Since observation is perpendicular to solution flow, the optical path length is determined by the width of the observation tube (0.212 cm). Reaction half-lives can be measured in the range of 0.07–3 ms.

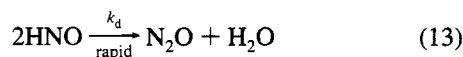
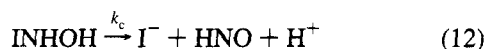
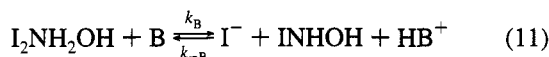
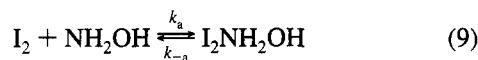
For pseudo-first-order reactions, the absorbance ( $A_p$ ) is measured at 128 positions along the observation cell, and these positions are converted to the appropriate time scale for each flow velocity. The apparent rate constant,  $k_{app}$ , is evaluated from plots of  $\ln(A_p - A_\infty)$  vs time for each of 126 different flow velocities. On the basis of earlier studies,<sup>22,23</sup> the physical mixing rate constant is proportional to the flow velocity ( $k_{mix} = k_m v$ ), and eq 6 relates the apparent rate constant to the chemical reaction rate constant ( $k_r$ ) and the mixing rate constant. A double reciprocal plot of  $1/k_{app}$  against  $1/v$  gives  $1/k_r$  as the intercept.

$$\frac{1}{k_{app}} = \frac{1}{k_m} \left( \frac{1}{v} \right) + \frac{1}{k_r} \quad (6)$$

## Results and Discussion

Rate constants for the loss of  $[I_2]_T$  are measured with variation of  $[NH_2OH]_T$ ,  $[I^-]$ ,  $[H^+]$ , and buffer concentrations. While we agree with earlier results that indicate the reactive species are  $I_2$  and  $NH_2OH$ , rather than  $I_3^-$  or  $NH_3OH^+$ , we observe four aspects of these reactions that had not been reported previously. (1) The reactions are general-base assisted, where  $CH_3COO^-$ ,  $NH_2OH$ ,  $HPO_4^{2-}$ , and  $OH^-$  accelerate the rate of loss of iodine. At high concentrations of hydroxylamine, the rate expression contains both  $[NH_2OH]$  and  $[NH_2OH]^2$  terms, because hydroxylamine acts as a nucleophile and as a general base. (2) Kinetic evidence is obtained for appreciable concentrations of a hydroxylamine–iodine adduct,  $I_2NH_2OH$ . (3) Kinetic evidence is found for INHOH as a steady-state species. (4) At low pH the rate is suppressed by  $[H^+]$  to a greater extent than can be attributed to  $NH_3OH^+$  formation. We also confirm an earlier observation<sup>7</sup> that at low pH the rate is suppressed by  $[I^-]$  concentration to a greater extent than can be attributed to  $I_3^-$  formation. The rate dependencies are moderately complicated, so we shall take the liberty of presenting all the steps in the proposed mechanism (eqs 7–13) before we show how it

### Proposed Mechanism



accounts for the results. At 25.0 °C and  $\mu = 0.50$  M, the value for  $K_1$  is  $721 \text{ M}^{-1}$ <sup>27</sup> and the value for  $K_p$  is  $1.01 \times 10^6 \text{ M}^{-1}$ .<sup>28</sup> The rate constant for  $I_3^-$  formation<sup>11</sup> in eq 7 is  $5.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and the protonation rate constant to give  $NH_3OH^+$  should be greater than  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>29</sup> so reactions 7 and 8 are in rapid equilibria. The dehydrative dimerization reaction in eq 13 is

**Table 1.** Effect of Hydrogen Ion and Iodide Ion Concentrations on the Observed Rate Constant at Low pH without Added Buffers<sup>a</sup>

| $[H^+]$ , mM | $[NH_2OH]_T$ , mM | $[I^-]$ , mM | $10^3 k_r$ , s <sup>-1</sup> |
|--------------|-------------------|--------------|------------------------------|
| 1.15         | 5.023             | 10.0         | 19.2                         |
| 2.88         | 5.023             | 10.0         | 5.66                         |
| 5.77         | 10.05             | 10.0         | 4.31                         |
| 7.21         | 5.023             | 10.0         | 1.65                         |
| 7.21         | 5.023             | 20.0         | 0.555                        |
| 9.90         | 5.019             | 3.00         | 5.69                         |
| 9.90         | 5.019             | 5.00         | 3.12                         |
| 9.90         | 5.019             | 8.00         | 1.83                         |
| 9.90         | 5.019             | 10.0         | 1.28                         |
| 9.90         | 5.019             | 13.0         | 0.837                        |
| 9.90         | 5.019             | 15.0         | 0.590                        |
| 9.90         | 5.019             | 18.0         | 0.509                        |
| 9.90         | 5.019             | 23.0         | 0.321                        |

<sup>a</sup> Conditions:  $25.0 \pm 0.1$  °C;  $[I_2]_T = 2.1 \times 10^{-5} \text{ M}$ ;  $\mu = 0.50 \text{ M}$  ( $\text{NaClO}_4$ ); rate constants are evaluated from single runs.

very fast; the value for  $k_d$  is reported to be  $(4.5 \pm 2.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>30</sup> If we assume that reaction 9 is in rapid equilibrium and treat INHOH as a steady-state species, the rate expression in eq 14 is obtained (where  $K_A = k_a/k_{-a}$ ). If  $K_a^{HB} = [H^+][B]/$

$$k_r = (k_b + \sum k_B[B])[NH_2OH]_T K_A k_c / (1 + K_p[H^+])(1 + K_1[I^-])(k_{-b}[I^-][H^+] + \sum k_{-B}[I^-][HB^+] + k_c) \quad (14)$$

$[HB^+]$ , it can be shown that  $k_{-B} = k_{-b} K_a^{HB} k_B / k_b$ , and this substitution in eq 14 gives eq 15. This mechanism assumes

$$k_r = (k_b + \sum k_B[B])[NH_2OH]_T K_A / (1 + K_p[H^+])(1 + K_1[I^-]) \left( \frac{k_{-b}}{k_c} [I^-][H^+] \left( 1 + \frac{\sum k_B[B]}{k_b} \right) + 1 \right) \quad (15)$$

that since the electron pair on the hydroxylamine nitrogen is the strongest Lewis base in the molecule, it will be used to form an  $I_2NH_2OH$  complex rather than the electron pair on oxygen, as implied by others.<sup>7,8</sup> Primary, secondary, and tertiary amines form adducts with iodine in *n*-heptane solutions.<sup>31,32</sup> A crystal structure has been determined for  $(CH_3)_3NI_2$ .<sup>33</sup> As mentioned previously, the rate of  $I_2$  adduct formation is extremely rapid, so we expect  $k_a$  to be near the diffusion-limiting value of  $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>10</sup> The rate-determining steps in the proposed mechanism are attributed to the formation and decay of INHOH.

**Kinetics at Low pH without Added Buffers.** The rate of loss of iodine in 9.90 mM  $[H^+]$  is relatively slow, and the rate constants decrease markedly as the  $I^-$  concentration increases (Table 1). Under these conditions, the general-base catalyzed pathway should be negligible and the  $\sum k_B[B]$  term can be deleted from eq 15. This leads to eq 16 as the expression for

$$k_r = k_b K_A [NH_2OH]_T / (1 + K_p[H^+])(1 + K_1[I^-]) \left( \frac{k_{-b}}{k_c} [I^-][H^+] + 1 \right) \quad (16)$$

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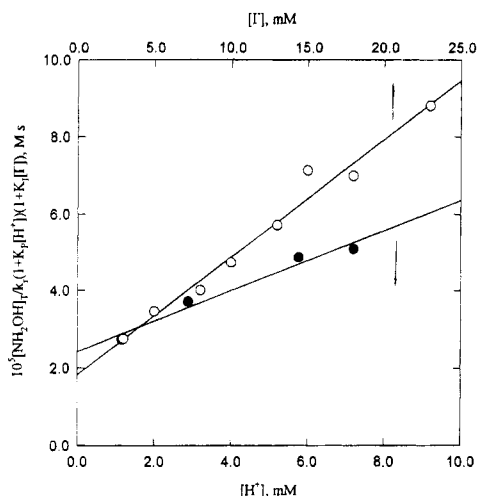
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(33) Strømme, K. O. *Acta Chem. Scand.* **1959**, *13*, 268–274.



**Figure 1.** Top abscissa: Dependence of the reciprocal of the observed rate constant in 9.9 mM  $[H^+]$  (corrected for the formation of  $NH_3OH^+$  and  $I_3^-$ ), on  $[I^-]$  (eq 17). The positive slope indicates additional suppression of the rate by  $I^-$  and gives  $k_{-b}/k_c = (1.7 \pm 0.3) \times 10^4 M^{-2}$  and  $k_b K_A = (5.5 \pm 1.1) \times 10^4 M^{-1} s^{-1}$ . Bottom abscissa: Dependence on  $[H^+]$  at constant  $[I^-]$  (10.0 mM). The positive slope indicates added suppression by  $[H^+]$  and gives  $k_{-b}/k_c = (1.6 \pm 0.1) \times 10^4 M^{-2}$  and  $k_b K_A = (4.1 \pm 0.3) \times 10^4 M^{-1} s^{-1}$ .

the observed first-order rate constant. Rearrangement of eq 16 gives eq 17, and the left-hand side is plotted against  $[I^-]$  in

$$\frac{[NH_2OH]_T}{k_t(1 + K_p[H^+])(1 + K_l[I^-])} = \frac{k_{-b}}{k_b K_A k_c} [I^-][H^+] + \frac{1}{k_b K_A} \quad (17)$$

Figure 1. Since the values of the ordinate are already corrected for suppression of the rate by  $I_3^-$  and  $NH_3OH^+$ , a horizontal line would be expected from previously proposed mechanisms.<sup>7,8</sup> However, the ordinate values (proportional to the reciprocal of  $k_t$ ) increase as  $[I^-]$  increases, which indicates that there is an additional source of  $I^-$  suppression of the reaction rate. We attribute this suppression to the reversibility of INHOH formation in eq 10 of the mechanism. These data give  $k_b K_A = (5.5 \pm 1.1) \times 10^4 M^{-1} s^{-1}$  and  $k_{-b}/k_c = (1.7 \pm 0.3) \times 10^4 M^{-2}$ .

Data in Table 1 also show that at low pH the  $k_t$  values decrease markedly as the  $[H^+]$  concentration increases. The effect is greater than can be attributed to the  $NH_3OH^+/NH_2OH$  equilibrium. Figure 1 shows a plot of the left-hand side of eq 17 against the  $[H^+]$  at constant  $[I^-]$ . These data give  $k_b K_A = (4.1 \pm 0.3) \times 10^4 M^{-1} s^{-1}$  and  $k_{-b}/k_c = (1.6 \pm 0.1) \times 10^4 M^{-2}$ . The additional suppression is again attributed to the reversibility of INHOH formation in eq 10. We consider the value of the intercept obtained from the  $[I^-]$  dependence in Figure 1 to be more reliable.

**Kinetics at pH 6 or Greater with Excess Hydroxylamine as a Buffer.** Under these conditions the rate of loss of  $I_3^-/I_2$  is too fast to measure by stopped-flow methods. Although the reactions are easily observed by the PAF method with integrating observation, we find that the apparent rate constants evaluated by eq 5 are not self-consistent as the concentration of  $NH_2OH$  and the pH are varied. In this equation,  $A_0$  is calculated for the postmixed  $I_3^-/I_2$  solution before it reacts with  $NH_2OH$ . If an extremely fast reaction occurs between  $I_2$  and  $NH_2OH$  to form  $I_2NH_2OH$  (as proposed in eq 9), the initial absorbance prior to the measured reaction may be significantly less than the assigned value because some  $I_3^-$  is instantaneously converted to  $I_2NH_2OH$ . As a consequence, the  $k_t$  value calculated from eq 5 will be too large. This error is inherent in

**Table 2.** Hydroxylamine and Hydroxide Ion Dependence Measured on the PAF-PRO<sup>a</sup>

| $[NH_2OH]_T$ , mM | p[H <sup>+</sup> ] | $10^{-3}k_t$ , s <sup>-1</sup> | $[NH_2OH]_T$ , mM | p[H <sup>+</sup> ] | $10^{-3}k_t$ , s <sup>-1</sup> |
|-------------------|--------------------|--------------------------------|-------------------|--------------------|--------------------------------|
| 10.12             | 6.00               | $0.618 \pm 0.003$              | 50.61             | 6.06               | $9.6 \pm 0.1$                  |
| 15.18             | 6.03               | $1.13 \pm 0.02$                | 20.00             | 6.21               | $2.92 \pm 0.06$                |
| 20.00             | 6.07               | $2.27 \pm 0.02$                | 20.00             | 6.34               | $3.6 \pm 0.1$                  |
| 25.31             | 6.04               | $2.88 \pm 0.05$                | 20.00             | 6.48               | $4.14 \pm 0.08$                |
| 30.37             | 6.04               | $3.86 \pm 0.07$                | 20.00             | 6.63               | $4.89 \pm 0.08$                |
| 40.49             | 6.05               | $6.02 \pm 0.04$                | 20.00             | 6.84               | $5.7 \pm 0.2$                  |

<sup>a</sup> Conditions:  $25.0 \pm 0.1$  °C;  $\mu = 0.50$  M (NaClO<sub>4</sub>);  $\lambda = 353$  nm;  $[I^-] = 20$  mM;  $[I_2]_T = 0.2$  mM. <sup>b</sup> The  $k_t$  values (average of four to five trials) are obtained from the double reciprocal relationship in eq 8, where  $k_{app}$  is the apparent first-order rate constant for the loss of  $I_3^-$ .

the integrating observation method, because the calculations are based on a single step process for observable reactants and products. (This PAF method can evaluate multistep mechanisms if the intermediates do not have appreciable concentrations or if additional information permits corrected values for  $A_0$ .)

The new PAF-PRO instrument avoids this problem. The progress of the reaction is observed perpendicular to the direction of flow, and the loss of absorbance of  $I_3^-$  is measured as the reaction mixture moves along the observation cell. Extremely fast reactions between  $I_2$  and  $NH_2OH$  to form appreciable amounts of  $I_2NH_2OH$  decrease the  $A_p$  values due to the initial  $I_3^-$  loss but do not otherwise affect the pseudo-first-order  $k_{app}$  values in the subsequent reactions. The  $k_{app}$  values are independent of  $A_0$ .

Table 2 shows that values of  $k_t$  increase from 618 to 9600 s<sup>-1</sup> as the  $[NH_2OH]_T$  increases from 10.1 to 50.6 mM at p[H<sup>+</sup>] =  $6.03 \pm 0.03$ . Table 2 also gives the dependence of  $k_t$  as the p[H<sup>+</sup>] values increase from 6.07 to 6.84 at constant  $[NH_2OH]_T$ . The absorbance changes measured with the PAF-PRO instrument indicate that appreciable amounts of  $I_2NH_2OH$  are formed prior to the observed reaction. The definition of  $[I_2]_T$  under these conditions is given by eq 18, where  $[I_2NH_2OH] =$

$$[I_2]_T = [I_2] + [I_3^-] + [I_2NH_2OH] \quad (18)$$

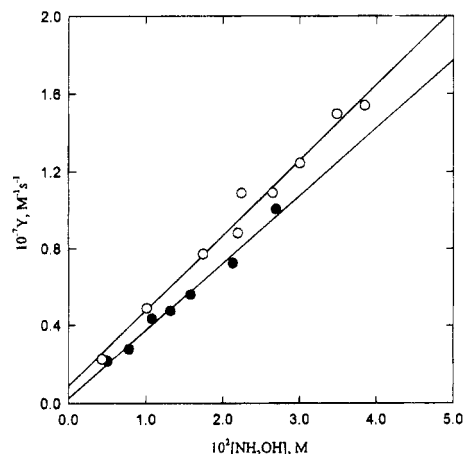
$K_A[NH_2OH][I_2]$ . (Since  $NH_2OH \cdot HCl$  was used, we also considered  $I_2Cl^-$  formation. However, its association constant is only  $1.7 M^{-1}$ ,<sup>34</sup> and the amount of  $I_2Cl^-$  present is negligible.) The rate expression in eq 15 can now be written in terms of eq 19, where the rate-determining step is the breakup of  $I_2NH_2-$

$$\frac{k_t(1 + K_p[H^+])(1 + K_l[I^-] + K_A[NH_2OH])}{[NH_2OH]_T} = (k_b + k_{NH_2OH}[NH_2OH] + k_{OH}[OH^-])K_A \quad (19)$$

OH (eqs 10 and 11) with negligible reversibility for these steps in the mechanisms at higher pH (i.e.,  $(k_{-b}/k_c)[I^-][H^+] \ll 1$ ). Data in Table 2 were analyzed with a nonlinear Marquadt-Levenberg algorithm<sup>35</sup> to calculate the best fit of the rate constants ( $k_{NH_2OH}$  and  $k_{OH}$ ) and the equilibrium constant ( $K_A$ ) to the relationship in eq 19, where a value of  $5.5 \times 10^4 M^{-1} s^{-1}$  for  $k_b K_A$  determined from the low pH data is used. The nonlinear fit yields the values of  $k_{NH_2OH} = (7.3 \pm 1.2) \times 10^5 M^{-1} s^{-1}$ ,  $k_{OH} = (1.9 \pm 0.7) \times 10^{10} M^{-1} s^{-1}$ , and  $K_A = k_a/k_{-a} = (4.8 \pm 1.3) \times 10^2 M^{-1}$ . These values are further confirmed by the linear fit illustrated in Figure 2, which shows

(34) Cason, D. L.; Neumann, H. M. *J. Am. Chem. Soc.* **1961**, *83*, 1822–1828.

(35) Sigma Plot, revision spw 1.02 July 1993, Jandel Scientific, San Rafael, CA.



**Figure 2.** PAF-PRO and PAF-IV data at  $p[H^+] = 6.03 \pm 0.03$  for the pseudo-first-order rate constants for the loss of  $[I_2]_T$  as a function of excess  $[NH_2OH]$ . The  $Y$  values are defined by the left-hand side of eq 19 where  $K_A = 480 \text{ M}^{-1}$ :  $\bullet$ , PAF-PRO data;  $\circ$ , PAF-IV data after correction of  $A_0$  based on  $K_A$ . The slope for the PAF-PRO data corresponds to  $k_{NH_2OH}K_A$  and gives a  $k_{NH_2OH}$  value of  $7.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

a plot of the left-hand side of eq 19 (defined as  $Y$ ) against the free  $NH_2OH$  concentration at constant  $p[H^+] = 6.03$ . The positive slope corresponds to contributions of  $[NH_2OH]^2$  to the overall rate, because hydroxylamine acts as both a nucleophile and a general base. The slope is  $3.5 \times 10^8 \text{ M}^{-2} \text{ s}^{-1} = k_{NH_2OH}K_A$ , and the intercept is  $2.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} = (k_b + k_{OH}[OH^-])K_A$ . This gives  $k_{NH_2OH} = 7.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_b = 115 \text{ s}^{-1}$  (from the evaluation of  $k_bK_A$  at low pH), and  $k_{OH} = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Data in Table 2 at constant  $[NH_2OH]_T$  and variable  $p[H^+]$  permit a value of  $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  to be calculated for  $k_{OH}$ . Despite the relatively small contribution of the  $k_{OH}[OH^-]K_A$  term to the observed rate constant, there is good agreement between the  $k_{OH}$  values from the intercept in Figure 2 and these data. It is difficult to use higher pH conditions for additional tests of the rate expression because of the lack of buffer capacity, the hydrolysis of  $I_2$ , and the extremely fast reactions. Proton-transfer rate constants to  $OH^-$  often exceed the diffusion limiting value due to hydrogen bonding, and values of  $(1-4) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  have been measured<sup>29</sup> for many weak acids.

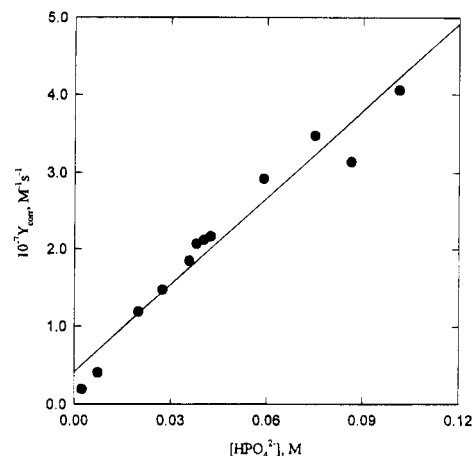
Once the  $K_A$  value is known, it is possible to correct the  $A_0$  values used for the PAF-IV calculations. (The absorbance contribution of  $I_2NH_2OH$  is assumed to be negligible compared to the absorbance of  $I_3^-$  at 353 nm, as is the case for  $I_2(aq)$  and  $I_2S_2O_3^{2-}$ .<sup>12</sup>) Although the corrections are large, Figure 2 shows that the corrected PAF-IV data give a slope of  $3.9 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$ , which is in reasonable agreement with the value of  $3.5 \times 10^8 \text{ M}^{-2} \text{ s}^{-1}$  obtained from the PAF-PRO experiments. We consider the PAF-PRO values to be more accurate; however, it is important to show the validity of this type of correction.

**Kinetics with Phosphate Buffer.** We found no evidence for a  $(I_2OPO_3H)^{2-}$  complex based on the lack of absorbance changes at 353 nm for a  $4.8 \times 10^{-5} \text{ M}$   $[I_2]_T$  solution in 20 mM  $I^-$  and 200 mM total phosphate buffer concentration ( $[PO_4]_T = [H_2PO_4^-] + [HPO_4^{2-}]$ ) at  $p[H^+] = 6.71$ . The PAF-IV method was used to study reactions with variation of the  $[PO_4]_T$  concentration from 12.5 to 188 mM at  $p[H^+] = 5.8$  to 6.5 and with  $[NH_2OH]_T$  concentrations of 2.5 and 10.0 mM,  $[I^-] = 10 \text{ mM}$ , and  $[I_2]_T = 2.1 \times 10^{-5} \text{ M}$ . The results given in Table 3 show that the corrections necessitated by  $A_0$  changes (due to  $I_2NH_2OH$  formation) result in only a 10–30% decrease of the  $k_r$  values. The  $k_r^{\text{corr}}$  values are reliable rate constants for the phosphate catalyzed reactions, and the results are shown in Figure 3 where  $Y_{\text{corr}}$  is given by eq 20 with  $K_A = 480 \text{ M}^{-1}$ .

**Table 3.** Phosphate Dependence Measured with the PAF-IV<sup>a</sup>

| $[PO_4]_T$ ,<br>mM | $p[H^+]$ | $[NH_2OH]_T$ ,<br>mM | $10^{-3}k_r$ , <sup>c</sup><br>$s^{-1}$ | $10^{-3}k_r^{\text{corr}}$ , <sup>d</sup><br>$s^{-1}$ |
|--------------------|----------|----------------------|-----------------------------------------|-------------------------------------------------------|
| 12.50              | 5.82     | 10.05                | 1.70                                    | 1.38                                                  |
| 25.00              | 6.08     | 10.05                | 4.18                                    | 3.17                                                  |
| 50.00              | 6.28     | 10.05                | 11.7                                    | 8.45                                                  |
| 62.50              | 6.35     | 10.05                | 14.9                                    | 10.6                                                  |
| 71.25              | 6.46     | 2.513                | 4.48                                    | 4.04                                                  |
| 77.50              | 6.44     | 2.513                | 4.92                                    | 4.44                                                  |
| 81.25              | 6.45     | 2.513                | 5.07                                    | 4.58                                                  |
| 83.75              | 6.47     | 2.513                | 5.24                                    | 4.72                                                  |
| 125.0              | 6.41     | 2.513                | 6.69                                    | 6.05                                                  |
| 150.0              | 6.46     | 2.513                | 8.18                                    | 7.38                                                  |
| 168.8              | 6.48     | 2.513                | 7.51                                    | 6.77                                                  |
| 187.5              | 6.53     | 2.513                | 9.91                                    | 8.90                                                  |

<sup>a</sup> Conditions:  $25.0 \pm 0.1^\circ \text{C}$ ;  $\mu = 0.50 \text{ M}$  ( $\text{NaClO}_4$ );  $\lambda = 353 \text{ nm}$ ;  $[I^-] = 0.010 \text{ M}$ ;  $[I_2]_T = 2.1 \times 10^{-5} \text{ M}$ . <sup>b</sup>  $[PO_4]_T = [HPO_4^{2-}] + [H_2PO_4^-]$ . <sup>c</sup>  $k_r$  values (four to five trials) measured from PAF-IV prior to the corrections for the decrease of  $A_0$ . <sup>d</sup>  $k_r^{\text{corr}} = k_r \times 8.21/(8.21 + K_A[NH_2OH])$ , where  $K_A = 480 \text{ M}^{-1}$ .



**Figure 3.** Hydrogen phosphate ion catalysis of the reaction between  $I_2$  and  $NH_2OH$  measured by the PAF-IV method with correction of  $A_0$  based on  $K_A = 480 \text{ M}^{-1}$ . The  $Y_{\text{corr}}$  value is given by eq 20. The slope equals  $k_{HPO_4}K_A$  and corresponds to a  $k_{HPO_4}$  value of  $7.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

The slope, which corresponds to  $k_{HPO_4}K_A$  (eq 21), equals  $3.7 \times$

$$Y_{\text{corr}} = \frac{k_r^{\text{corr}}(1 + K_p[H^+])(1 + K_I[I^-] + K_A[NH_2OH])}{[NH_2OH]_T} - \frac{k_{OH}K_A[OH^-] - k_{NH_2OH}K_A[NH_2OH]}{[NH_2OH]_T} \quad (20)$$

$$Y_{\text{corr}} = k_{HPO_4}K_A[HPO_4^{2-}] + k_bK_A \quad (21)$$

$10^8 \text{ M}^{-2} \text{ s}^{-1}$ ; therefore,  $k_{HPO_4} = 7.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . It should be noted that the values for  $k_{NH_2OH}$  and  $k_{HPO_4}$  are similar, as expected for general-base catalysis by bases of similar strength.

**Kinetics with Acetate Buffer.** Stopped-flow methods (Table 4) are used to measure the reaction rates from  $p[H^+] = 3.4$  to 5.0 in 0.20 M total acetate ( $[HOAc]_T = [OAc^-] + [HOAc]$ ), with 10 mM  $[NH_2OH]_T$ , 10 mM  $[I^-]$ , and  $2.1 \times 10^{-5} \text{ M}$   $[I_2]_T$ . The  $k_r$  values are dependent on the  $[H^+]$  concentration as well as the acetate concentration, and all the mechanistic steps in eqs 7–13 must now be considered. If  $Y$  is defined by the left-hand side of eq 19, its dependence is given by eq 22, where B

$$Y = (k_b + \sum k_B[B])K_A / \left[ \frac{k_{-b}}{k_c} [I^-][H^+] \left( 1 + \frac{\sum k_B[B]}{k_b} \right) + 1 \right] \quad (22)$$

is  $OAc^-$ ,  $NH_2OH$ , and  $OH^-$ . The value of  $k_{OAc}$  ( $2.3 \times 10^4$

**Table 4.**  $p[H^+]$  Dependence in Acetate Buffer Measured by Stopped-Flow Methods<sup>a</sup>

| $p[H^+]$ | $[NH_2OH]_T$ , mM | $k_r$ , $s^{-1}$  | $p[H^+]$ | $[NH_2OH]_T$ , mM | $k_r$ , $s^{-1}$ |
|----------|-------------------|-------------------|----------|-------------------|------------------|
| 3.44     | 10.13             | $0.851 \pm 0.008$ | 4.49     | 9.802             | $40.9 \pm 0.4$   |
| 3.67     | 10.13             | $2.22 \pm 0.002$  | 4.57     | 9.802             | $53.8 \pm 0.7$   |
| 3.82     | 10.13             | $3.89 \pm 0.13$   | 4.66     | 9.802             | $71.9 \pm 0.7$   |
| 4.00     | 10.13             | $8.22 \pm 0.11$   | 4.76     | 9.802             | $99 \pm 1$       |
| 4.18     | 10.13             | $16.2 \pm 0.4$    | 4.87     | 9.802             | $139 \pm 3$      |
| 4.27     | 10.13             | $23.1 \pm 0.3$    | 4.98     | 9.802             | $196 \pm 6$      |

<sup>a</sup> Conditions:  $25.0 \pm 0.1$  °C;  $\mu = 0.50$  M (NaClO<sub>4</sub>);  $\lambda = 353$  nm;  $[I^-] = 0.010$  M;  $[I_2]_T = 2.1 \times 10^{-5}$  M;  $[HOAc]_T = 0.20$  M.

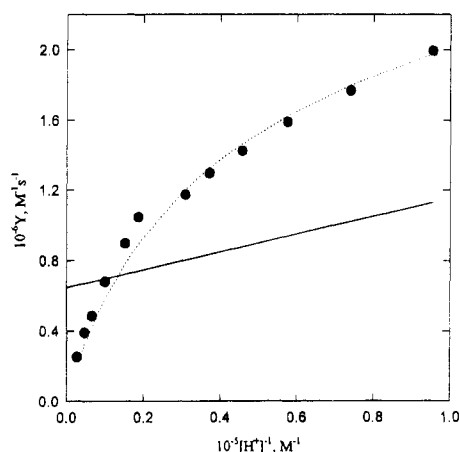
<sup>b</sup> Experimental stopped-flow rate constants ( $k_{\text{expt}}$ ) larger than  $50$  s<sup>-1</sup> were corrected for mixing limitations of the instruments by using  $k_r = k_{\text{expt}}/(1 - (k_{\text{expt}}/k_{\text{mix}}))$ , where  $k_{\text{mix}} = 2900$  s<sup>-1</sup> for the Hi-Tech and  $k_{\text{mix}} = 5276$  s<sup>-1</sup> for the Durrum.

**Table 5.** Summary of Equilibrium and Rate Constants<sup>a</sup>

| con-<br>stant | value                                                     | con-<br>stant | value                                                           |
|---------------|-----------------------------------------------------------|---------------|-----------------------------------------------------------------|
| $K_I$         | $721 \text{ M}^{-1}$ <sup>b</sup>                         | $k_{NH_2OH}$  | $(7.3 \pm 1.2) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$       |
| $K_p$         | $1.01 \times 10^6 \text{ M}^{-1}$ <sup>c</sup>            | $k_{HPO_4}$   | $(7.7 \pm 0.4) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$       |
| $K_A$         | $(4.8 \pm 1.3) \times 10^2 \text{ M}^{-1}$                | $k_{OH}$      | $(1.9 \pm 0.7) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$    |
| $k_a$         | $\sim 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$        | $k_{-b}/k_c$  | $(1.7 \pm 0.2) \times 10^4 \text{ M}^{-2}$                      |
| $k_b$         | $(1.15 \pm 0.23) \times 10^2 \text{ s}^{-1}$              | $k_d$         | $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>d</sup> |
| $k_{OAc}$     | $(2.3 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ |               |                                                                 |

<sup>a</sup> Conditions:  $25.0$  °C;  $\mu = 0.50$  M. <sup>b</sup> Reference 27. <sup>c</sup> Reference 28.

<sup>d</sup> Reference 30.



**Figure 4.** Stopped-flow data for the rate dependence on  $1/[H^+]$  in acetate buffer, where the experimental points for  $k_r$  are converted to  $Y$  as defined by the left-hand side of eq 19, and the dashed line shows the fit of  $Y$  to eq 22. This gives a rate constant of  $2.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for the acetate ion reaction with  $I_2NH_2OH$ . The solid line shows the failure of the predicted dependence given in ref 8, where the ordinate is  $k_r(1 + K_p[H^+])(1 + K_I[I^-])/[NH_2OH]_T$ .

$\text{M}^{-1} \text{ s}^{-1}$ ) was determined from the fit<sup>35</sup> of the data (Table 4) to eq 22, where  $K_A = 480 \text{ M}^{-1}$ ,  $k_b = 115 \text{ s}^{-1}$ ,  $k_{-b}/k_c = 1.7 \times 10^4 \text{ M}^{-2}$ ,  $k_{NH_2OH} = 7.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{OH} = 1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . Figure 4 shows the fit of the  $Y$  term plotted against  $1/[H^+]$ . The dependence predicted from the paper by Wang et al.<sup>8</sup> is shown for comparison. They were not aware that acetate ion assisted the rate and that there was additional suppression by  $[I^-]$  and  $[H^+]$ .

#### Rejection of Another General-Base-Assisted Mechanism.

An alternative mechanism was considered in which base-assisted decomposition of  $INHOH$  occurs (eq 23) rather than the



corresponding reaction of  $I_2NH_2OH$  as proposed in eq 11. At

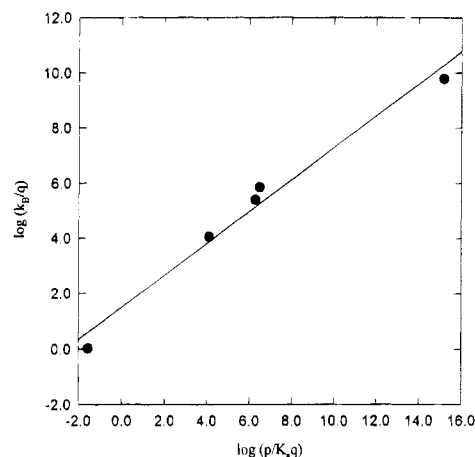
**Table 6.** Brønsted–Pedersen Relationship<sup>a</sup>

| B                              | $pK_a(HB^+)$       | $p^b$ | $q^c$ | $\log(k_B/q)$ | $\log(p/qK_A)$ |
|--------------------------------|--------------------|-------|-------|---------------|----------------|
| H <sub>2</sub> O               | -1.73 <sup>a</sup> | 3     | 2     | 0.021         | -1.55          |
| OAc <sup>-</sup>               | 4.41 <sup>d</sup>  | 1     | 2     | 4.06          | 4.11           |
| NH <sub>2</sub> OH             | 6.0 <sup>e</sup>   | 3     | 1     | 5.86          | 6.48           |
| HPO <sub>4</sub> <sup>2-</sup> | 6.46 <sup>f</sup>  | 2     | 3     | 5.41          | 6.28           |
| OH <sup>-</sup>                | 15.34 <sup>g</sup> | 2     | 3     | 9.80          | 15.16          |

<sup>a</sup> Reference 36. <sup>b</sup>  $p$  is the number of equivalent proton sites on  $HB^+$ .

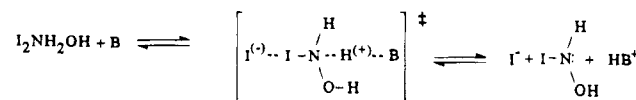
<sup>c</sup>  $q$  is the number of equivalent basic sites on B. <sup>d</sup> Reference 40.

<sup>e</sup> Reference 28. <sup>f</sup> Reference 41. <sup>g</sup> Reference 42.



**Figure 5.** Brønsted–Pedersen plot of the rate constants for the general-base-assisted proton-transfer reactions with  $I_2NH_2OH$ . The slope ( $\beta$ ) is 0.58.

#### Scheme 1



low pH without added buffers, the alternative mechanism gives exactly the same expression for  $k_r$  found in eq 16. At high pH and high buffer concentrations, the  $Y$  term (defined by the left-hand side of eq 19) would now be expressed by eq 24. Since  $(k_{-b}/k_c)[I^-][H^+] \ll 1 + (k_c^B[B]/k_c)$ , it follows that  $Y = k_bK_A$  and there would be no general-base assistance. Therefore, the alternative mechanism is not suitable.

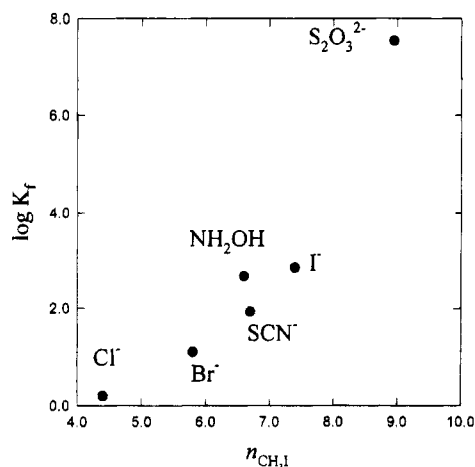
$$Y = \left( 1 + \frac{\sum k_c^B[B]}{k_c} \right) k_b K_A / \left[ \frac{k_{-b}}{k_c} [I^-][H^+] + 1 + \frac{\sum k_c^B[B]}{k_c} \right] \quad (24)$$

**Brønsted–Pedersen Relationship.** Table 6 summarizes the  $pK_a$  values for  $HB^+$  and shows the statistical corrections used for the Brønsted–Pedersen plot<sup>36</sup> in Figure 5. The  $k_B$  value for H<sub>2</sub>O equals  $k_b/55.5 = 2.1 \text{ M}^{-1} \text{ s}^{-1}$ . (Other  $k_B$  values are given in Table 5.) The slope for this plot gives  $\beta = 0.58$ ; this indicates a transition state shown in Scheme 1 in which there is a significant degree of proton transfer from  $I_2NH_2OH$  to B as  $I^-$  leaves to give  $HB^+ + INHOH + I^-$ .

**Adducts of  $I_2$  with Nucleophiles.** Stability constants ( $K_f$ ) for adduct formation between  $I_2(aq)$  and various nucleophiles increase greatly with an increase in the nucleophilicity of the Lewis bases.<sup>12</sup> Figure 6 shows the correlation of  $\log K_f$  values with the values for the  $n_{CH_3I}$  nucleophilic reactivity constants.<sup>37</sup> A  $n_{CH_3I}$  value of 6.60 is reported<sup>37</sup> for  $NH_2OH$ , and we use our

(36) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, 1973; p 198.

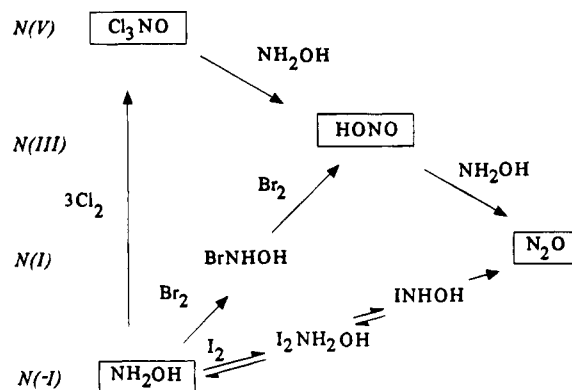
(37) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am. Chem. Soc.* **1968**, *90*, 319–326.



**Figure 6.** Dependence of the stability constants ( $K_f$ ) of  $\text{I}_2$  adducts in aqueous solution (25.0 °C) on the nucleophilic reactivity constant<sup>37</sup> of Lewis bases.

kinetically determined value of  $480 \text{ M}^{-1}$  for the  $K_f$  value of  $\text{I}_2\text{NH}_2\text{OH}$ . There is a great deal of scatter for the correlation in Figure 6, but it can be seen that strong adduct formation is to be expected between  $\text{I}_2$  and  $\text{NH}_2\text{OH}$ . Hydroxylamine nucleophilic interactions are enhanced by the  $\alpha$  effect,<sup>38,39</sup> added reactivity due to the presence of an unshared pair of electrons on the atom  $\alpha$  to the donor atom. The Brønsted basicities of  $\text{HPO}_4^{2-}$  and  $\text{NH}_2\text{OH}$  are similar, but  $\text{NH}_2\text{OH}$  is a much stronger Lewis base and we find no evidence of adduct formation between  $\text{HPO}_4^{2-}$  and  $\text{I}_2$ . This is consistent with our assignment of  $\text{I}_2\text{NH}_2\text{OH}$  as the intermediate as opposed to  $\text{NH}_2\text{OI}_2^-$ .<sup>8</sup>

**Summary.** Iodine oxidation of hydroxylamine has a complex rate expression that is first order in  $[\text{I}_2]_T$  with suppression by  $[\text{I}^-]$ ,  $[\text{I}^-]^2$ ,  $[\text{H}^+]$ ,  $[\text{H}^+]^2$ , and  $[\text{HOAc}]$  and with acceleration by  $[\text{NH}_2\text{OH}]$ ,  $[\text{NH}_2\text{OH}]^2$ ,  $[\text{OAc}^-]$ ,  $[\text{HPO}_4^{2-}]$ , and  $[\text{OH}^-]$ . Despite its complexity, this rate dependence corresponds to a straightforward mechanism (eqs 7–13) with an  $\text{I}_2\text{NH}_2\text{OH}$  adduct that reacts by general-base assistance to form  $\text{INHOH}$  as a steady-state intermediate. The decomposition of  $\text{INHOH}$  gives nitrosyl hydride ( $\text{HNO}$ ) which undergoes rapid dehydrative dimerization to give  $\text{N}_2\text{O}$ . The equilibrium and rate constants for eqs 7–13 are summarized in Table 5 and give excellent fits of the data over an enormous range ( $4 \times 10^7$ -fold) of observed first-order rate constants. The ability to fit the complex rate dependence under all these conditions lends strong support to the validity of the mechanism. The overall process corresponds to an  $\text{I}^+$



**Figure 7.** Different initial products of halogen oxidation of hydroxylamine. Three  $\text{Cl}_2$  react in rapid succession to give a  $\text{N(V)}$  species that is subsequently reduced by excess  $\text{NH}_2\text{OH}$ , first to  $\text{N(III)}$  and then to  $\text{N(I)}$ . Two  $\text{Br}_2$  react in rapid succession to give  $\text{N(III)}$  before a slower reduction gives  $\text{N(I)}$ . One  $\text{I}_2$  reacts to give  $\text{N(I)}$  with kinetic evidence for  $\text{I}_2\text{NH}_2\text{OH}$  and  $\text{INHOH}$  intermediates. In the presence of excess  $\text{NH}_2\text{OH}$  the final product is  $\text{N}_2\text{O}$  for all three halogens.

transfer to nitrogen followed by  $\text{I}^-$  loss from nitrogen to increase the oxidation state from  $\text{N(-I)}$  to  $\text{N(+I)}$ . A recent study<sup>13</sup> of electron-transfer reactions for the  $\text{NH}_2\text{OH}/\text{NH}_2\text{OH}^+$  redox couple gives an estimated self-exchange rate constant of  $5 \times 10^{-13} \text{ M}^{-1} \text{ s}^{-1}$  and a giant reorganizational energy for this couple. Therefore, electron-transfer rates will be very slow. This is consistent with our evidence that ion-transfer reactions occur rather than electron-transfer reaction.

**Comparison of Halogen Oxidations of Hydroxylamine.** The  $\text{Cl}_2$  reactions were studied<sup>4</sup> from  $\text{p}[\text{H}^+]$  0 to 1, and a rate constant of  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was found for the first step in the reaction between  $\text{Cl}_2$  and  $\text{NH}_2\text{OH}$ . A  $\text{ClNHOH}$  intermediate was proposed to react rapidly with two more  $\text{Cl}_2$  to give  $\text{Cl}_3\text{NO}$  as the first product (Figure 7). The  $\text{Br}_2$  reactions were studied<sup>5</sup> from  $\text{p}[\text{H}^+]$  0 to 6, and a rate constant of  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was found for the reaction between  $\text{Br}_2$  and  $\text{NH}_2\text{OH}$ . A  $\text{BrNHOH}$  intermediate was proposed that reacts rapidly with a second  $\text{Br}_2$  to give  $\text{HONO}$  as the first product. The corresponding reaction between  $\text{I}_2$  and  $\text{NH}_2\text{OH}$  to give  $\text{INHOH}$  is much slower with a rate constant ( $K_A k_b$ ) of  $5.5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  when it is not base-assisted. In the presence of high concentrations of phosphate buffer, the  $\text{I}_2$  reaction with  $\text{NH}_2\text{OH}$  is several orders of magnitude faster. There is excellent kinetic evidence for the presence of appreciable concentrations of  $\text{I}_2\text{NH}_2\text{OH}$  and for the existence of  $\text{INHOH}$  as a steady-state intermediate. In excess  $\text{NH}_2\text{OH}$  the product is  $\text{N}_2\text{O}$ . As shown in Figure 7,  $\text{N}_2\text{O}$  is the eventual product for all three halogen oxidations when excess  $\text{NH}_2\text{OH}$  is present.

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