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Kinetics and Mechanisms of the Oxidation of Hydrazinium Ion ($N_2H_5^+$) by ICl and IBr; Determination of the Protonation Constant of $N_2H_5^+$

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The kinetics of $N_2H_5^+$ oxidation by ICl and IBr in 0.1−1.0 M [H^+] is investigated by following the formation of I_2Cl^- and I_2Br^- with excess ICl_2^- and IBr_2^-, respectively, when total hydrazine is the limiting reactant. Highly acidic solutions are needed to suppress the rates of N_2H_4 reactions and to avoid hydrolysis of the interhalogens. Protonation constants of $N_2H_5^+$, $K_{P2} = [N_2H_6^{2+}]/[N_2H_5^+][H^+]$, measured spectrophotometrically at 25.0 °C with picric acid as an indicator, are 1.61 M^{-1} ($\mu = 0.50$ M) and 1.72 M^{-1} ($\mu = 1.00$ M). In the proposed mechanisms, ICl and IBr react by an I^+ transfer process to $N_2H_5^+$ with loss of H^+ (k_1) to form a steady-state species, $IN_2H_4^+$, that eliminates I^- and H^+ to give $N_2H_3^+$ (k_2). Subsequent reactions consume a second interhalogen, as diazine (N_2H_2) is rapidly oxidized to N_2. Rate constants (25.0 °C, $\mu = 1.00$ M) for the ICl/$N_2H_5^+$ reaction are $k_1 = 4.12 \times 10^6$ M^{-1} s^{-1}, $k_{-1}/k_2 = 1.9$ M^{-2} and for the IBr/$N_2H_5^+$ reaction are $k_1 = 7.6 \times 10^4$ M^{-1} s^{-1}, $k_{-1}/k_2 = 28$ M^{-2}. The relative rates of oxidation of $N_2H_5^+$ are ICl ≫ IBr ≫ I_2.

Introduction

Interhalogens can be used as titrants for chemical analysis of hydrazine and other reducing agents and as halogenation agents.[1−9] In general, the oxidation of hydrazine by halogens and interhalogens follow the stoichiometry in eq 1, where XY = I_2, Br_2, Cl_2, BrCl, IBr, and ICl.

$$N_2H_5^+ + 2XY \rightarrow N_2 + 2X^- + 2Y^- + 5H^+ \qquad (1)$$

However, the titration reaction of hydrazine by ICl is complicated due to the rapid reaction of the titrant, ICl, with the initial product, I^-, to form I_2Cl^-.[5−9]

For halogen reactions, only the oxidation of hydrazine by I_2 has been studied in detail. Liu and Margerum[10] recently proposed a mechanism for the oxidation of hydrazine by I_2 and gave evidence for the formation of a $I_2N_2H_4$ complex along with subsequent kinetic evidence of a steady-state species, $IN_2H_4^+$. However, little was known about the kinetics and mechanisms of the oxidation of hydrazine by ICl and IBr. Radhakrishnamurty and co-workers[11] reported the oxidation of hydrazinium ion by IBr in the presence of Hg(II) in $HOAc/OAc^-$ media. However, the reaction system was completely altered due to the possible formation of $IBrHg^{II}$ and Hg^{II}-N_2H_4 complexes. The conditions employed were limited to avoid precipitation of HgIBr and no kinetic data were obtained for the direct reaction between IBr and $N_2H_5^+$.

In the previous study of hydrazine reactions with iodine,[10] excess hydrazine concentrations were used and the reactions were studied from pH 0.35 to 8.0. Above pH 6.0, the very fast reactions were measured by the pulsed-accelerated-flow (PAF) method.[12] This work showed that N_2H_4 reacts 10^7 times faster than $N_2H_5^+$. Our present results show that ICl and IBr are much more reactive than I_2 with $N_2H_5^+$ and their reactions with N_2H_4 are too fast to measure even by the PAF method. Therefore, high acid concentrations are used, where the N_2H_4 concentration is negligible ($<10^{-12}$ M) and $N_2H_5^+$ is the reactant. At high H^+ concentrations, the reactions are suppressed because $N_2H_6^{2+}$ is not reactive. Acidic solutions are needed to prevent hydrolysis of the interhalogens.[13,14] High concentrations of X^- (X = Cl and Br) also suppress the rates because ICl_2^- and IBr_2^- are not reactive. The formation constant of ICl_2^-, $K_{ICl_2} = [ICl_2^-]/[ICl][Cl^-]$, is 76.9 M^{-1}.[13] The formation constant of IBr_2^-, $K_{IBr_2} = [IBr_2^-]/[IBr][Br^-]$, is 286 M^{-1}.[14]

Hydrazine is a moderate base and can form two protonated species, $N_2H_5^+$ and $N_2H_6^{2+}$. The first protonation constant of N_2H_4, K_{P1}, was measured by potentiometric titration and has a value of 1.15×10^8 M^{-1} at $\mu = 0.50$ M, 25.0 °C.[10] However, the measurement of the second protonation constant (K_{P2}) to give $N_2H_6^{2+}$ is difficult because $N_2H_5^+$ is a very weak base. Literature values for K_{P2} are not in agreement and range from 0.09 to 1.9 M^{-1} at different ionic strengths and temperatures.[15] According to Stanbury,[16] the weight of evidence supports a pK_a

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near −0.5, which corresponds to a K_{P2} of 3 M^{-1}. Higginson and Wright[15a] estimated the K_{P2} value of $N_2H_5^+$ to be 0.2 M^{-1} at 60 °C with $\mu = 3.5$ M by using a spectrophotometric method with picric acid as an indicator. In the present work, protonation constants of $N_2H_5^+$ at 25.0 °C and at two ionic strengths (μ = 0.50 and 1.00 M) are determined by a similar method. However, the dissociation constant and molar absorptivities of picric acid must be known under the same conditions in order to measure K_{P2} accurately. The dissociation constant of picric acid was previously determined by spectrophotometric and conductance methods.[17−19] The literature values of K_a, extrapolated to μ = 0 M, range from 0.2 to 0.6 M.[17] The molar absorptivities and dissociation constants of picric acid at 25.0 °C, μ = 0.50 and 1.00 M are measured in this work.

Experimental Section

Reagents. Solutions were prepared with doubly deionized, distilled water which was purged with argon. All chemicals used are analytical reagent grade. The ionic strength (μ) was adjusted with aqueous $NaClO_4$ that was recrystallized from water. "Bromide-free" hydrochloric acid was prepared by boiling 1500 mL of 20% HCl (diluted from concentrated HCl) with 0.5 g of $KMnO_4$ for 1 h to remove Cl_2, Br_2, I_2, and related interhalogens.[20] Hydrochloric acid was then distilled from this solution. The Br^- concentration in 1.0 M purified HCl was determined to be less than 8×10^{-8} M by following the absorbance of $BrCl_2^-$ (ϵ_{BrCl_2} = 32 700 M^{-1} cm^{-1} at 232 nm) after the addition of chlorine.[21] (Prior to the purification, the Br^- level was 1.0×10^{-5} M in 1.0 M HCl.) "Bromide-free" NaCl was prepared by the reaction of NaOH solution with "bromide-free" HCl. Solid NaCl was recrystallized from the slightly acidic solution and dried at 120 °C. The stock solution of NaCl was standardized gravimetrically.

Solutions of ICl_2^- were prepared by acidifying a stoichiometric mixture of NaI and KIO_3 with HCl.[13,22] Solutions of IBr_2^- were prepared from a stoichiometric mixture of NaI, KIO_3, $HClO_4$, and NaBr.[14] The reactions are described in eq 2.

$$2I^- + IO_3^- + 6H^+ + 6X^- \rightarrow 3IX_2^- + 3H_2O \ (X = Cl, Br) \qquad (2)$$

The stock solutions of NaI and NaBr were standardized by precipitation titration with standard 0.1 M $AgNO_3$ using 0.1% eosin as an indicator.[23] The stock solution of $HClO_4$ was prepared from 70% $HClO_4$ which was purged with argon both before and after the dilution to remove trace oxidant.[22]

Solutions of $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot H_2SO_4$ were used in the ICl and IBr reactions, respectively. These solutions were standardized with 0.025 M KIO_3 solution, which was prepared from a primary standard KIO_3 (dried at 130 °C).[24] Solutions of $HClO_4$, HCl, and picric acid were standardized against NaOH, which in turn was standardized with primary standard potassium hydrogen phthalate. A stock solution of 0.010 M picric acid was prepared from pure crystals (99+%). Dilute solutions of picric acid were standardized spectrophotometrically in 0.01 M NaOH solution at 355 nm by using our molar absorptivity value for the picrate ion (1.388×10^4 M^{-1} cm^{-1}).

Methods. For the determination of dissociation constant (K_a) of picric acid, a series of solutions was prepared with different $[H^+]$ and the same picric acid concentration at constant ionic strength. For the determination of protonation constant (K_{P2}) of $N_2H_5^+$, a series of solutions was prepared with different $[N_2H_5^+]_T$, the same initial $[HClO_4]$, and the same picric acid concentration at constant ionic strength. Spectrophotometric measurements were made for each solution (1 cm cell) with a Perkin-Elmer Lambda-9 UV/vis/NIR spectrophotometer interfaced to a Zenith 386/20 computer at 25.0 ± 0.1 °C. Spectral data from 200 to 500 nm were obtained with a scan rate of 120 nm/min and a slit width of 2 nm.

Kinetic studies for the reactions of $N_2H_5^+$ with ICl and IBr were performed on the Durrum stopped-flow spectrophotometer (Model DS110, optical path length = 1.71 cm) interfaced to a Zenith 286 PC with a Metrabyte A/D card. The reactions of $N_2H_5^+$ with ICl and IBr were observed under pseudo-first-order conditions by following the formation of I_2Cl^- at 275, 450, and 455 nm (ϵ_{I_2Cl} = 55000 M^{-1} cm^{-1} at 248 nm)[25] with excess ICl_2^- and the formation of I_2Br^- at 440 nm (ϵ_{I_2Br} = 2700 M^{-1} cm^{-1})[14] with excess IBr_2^-, respectively. Each kinetic trace was an average of at least four runs. All reactions were run at 25.0 ± 0.1 °C and 1.00 M ionic strength.

Results and Discussion

Determination of $N_2H_5^+$ Protonation Constant, K_{P2}. Values for K_{P2} are measured spectrophotometrically at two ionic strengths with picric acid as an indicator. The reasons for choosing picric acid as the indicator are (1) hydrazine does not have a distinct UV/vis spectrum,[26] (2) picric acid is very stable in hydrazine solution,[27] (3) picric acid and $N_2H_6^{2+}$ have similar acid strength, and (4) picrate ion has an intense UV/vis absorption band at 355 nm. Picric acid (HPi) dissociates into H^+ and picrate ion (Pi^-) in the solution (eq 3). In highly acidic solutions, hydrazine is present as $N_2H_5^+$ and $N_2H_6^{2+}$ (eq 4). Competition between picric acid (HPi) and $N_2H_5^+$ is described in eq 5. However, the molar absorptivities (ϵ_{Pi}, ϵ_{HPi}) and K_a of picric acid must be determined. Spectra of picric acid taken by changing $[H^+]$ (0.0398−0.9940 M $HClO_4$) at constant ionic strength show a very well-marked isosbestic point at 308 nm. A curve-fitting program with a Marquardt−Levenberg algorithm (SigmaPlot)[28] was used to fit the absorbance (A_λ) dependence on $[H^+]$ according to eq 6.

$$\mathrm{HPi} \overset{K_a}{\rightleftharpoons} H^+ + Pi^- \qquad (3)$$

$$N_2H_5^+ + H^+ \overset{K_{P2}}{\rightleftharpoons} N_2H_6^{2+} \qquad (4)$$

$$\mathrm{HPi} + N_2H_5^+ \rightleftharpoons Pi^- + N_2H_6^{2+} \qquad (5)$$

$$A_\lambda = \frac{(\epsilon_{Pi}K_a + \epsilon_{HPi}[H^+])[HPi]_T}{K_a + [H^+]} \qquad (6)$$

At μ = 1.00 M and 25.0 °C, results give K_a = 0.635 ± 0.005 M, $\epsilon_{HPi} = (2.23 \pm 0.04) \times 10^3$ M^{-1} cm^{-1}, and $\epsilon_{Pi} = (1.388 \pm 0.001) \times 10^4$ M^{-1} cm^{-1} at 355 nm. A K_a value of 0.610 ± 0.007 M is obtained at 285 nm. At μ = 0.50 M and 25.0 °C, results give K_a = 0.786 ± 0.002 M using the same ϵ_{HPi} and ϵ_{Pi}

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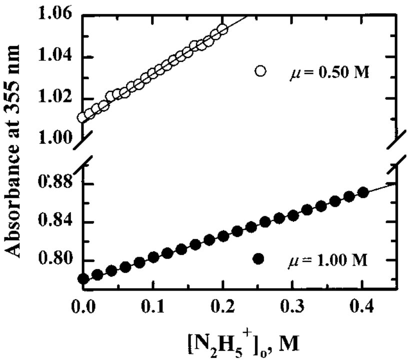

Figure 1. Fit of the absorbance changes (355 nm) of picric acid vs $[N_2H_5^+]_o$ for the determination of K_{P2} at 25.0 °C. Conditions: Cell path = 1 cm; (○) $\mu = 0.50$ M, $[HClO_4]_o = 0.2982$ M, $[N_2H_5^+]_o = 0-0.2008$ M, $[HPi]_T = 9.451 \times 10^{-5}$ M. Result: $K_{P2} = 1.61 \pm 0.02$ M^{-1}. (●) $\mu = 1.00$ M, $[HClO_4]_o = 0.5964$ M, $[N_2H_5^+]_o = 0$ to 0.4020 M, $[HPi]_T = 9.456 \times 10^{-5}$ M. Result: $K_{P2} = 1.72 \pm 0.01$ M^{-1}.

values obtained at $\mu = 1.00$ M. It is interesting that very similar values of K_a are obtained at 285, 345, 350, 360, and 370 nm, but the values decrease above 380 nm. The band at 355 nm has been assigned to the transitions involving the benzenoid and *p*-quinonoid states of the picrate ion, whereas the band at 400 nm has been attributed to the *o*-quinonoid states.[29] Our studies indicate that the *o*-quinoid states are more sensitive to the medium effects than the *p*-quinoid state. Therefore, the wavelength of 355 nm was used for both the determination of the K_a value of picric acid and the K_{P2} value of $N_2H_5^+$.

For the determination of K_{P2}, increases in absorbance at 355 nm (due to eq 5) were measured by adding $N_2H_4{\cdot}HCl$ to the picric acid solutions (initial $[H^+]_o$ are 0.2982 M for $\mu = 0.50$ and 0.5964 M for $\mu = 1.00$ M). The quadratic expression (eq 7) from eq 4 is needed to calculate $[H^+]$. The absorbance values

$$[H^+] = \frac{([H^+]_o - [N_2H_5^+]_o)K_{P2} - 1 + \sqrt{[([N_2H_5^+]_o - [H^+]_o)K_{P2} + 1]^2 + 4[H^+]_oK_{P2}}}{2K_{P2}} \qquad (7)$$

were corrected for the very small background absorbance due to $NaClO_4$ and $N_2H_4{\cdot}HCl$. The K_{P2} values are obtained by curve-fitting the absorbance of picric acid at 355 nm vs $[N_2H_5^+]_o$, in accord with eqs 6 and 7 by using the ϵ_{HPi}, ϵ_{Pi}, and K_a values of picric acid obtained at $\mu = 0.50$ and 1.00 M, respectively. Results from Figure 1 give values of K_{P2} (at 25.0 °C) 1.61 ± 0.02 M^{-1} at $\mu = 0.50$ M and 1.72 ± 0.01 M^{-1} at $\mu = 1.00$ M. These are somewhat smaller than the values estimated by Stanbury.[16]

Reactants and Products. For the reactions of IX/IX_2^- (X = Cl, Br) with $N_2H_5^+/N_2H_6^{2+}$, the products depend on the reactant that is in excess. When $[N_2H_5^+]_T$ is in excess, two reactions can occur. The initial reaction is

$$N_2H_5^+ + 4IX_2^- \rightarrow N_2 + 2I_2X^- + 6X^- + 5H^+ \qquad (8)$$

and the subsequent slower reaction is

$$2I_2X^- + N_2H_5^+ \rightarrow N_2 + 4I^- + 2X^- + 5\,H^+ \qquad (9)$$

Two steps are seen and the resulting kinetics are complex. When IX_2^- is in excess, the stoichiometry is the same as eq 8.

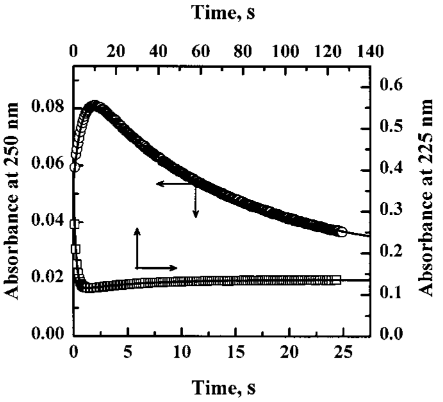

Figure 2. Kinetic traces for the reaction of ICl with excess $N_2H_5^+$ at 225 nm (□) and 250 nm (○). Conditions: 25.0 °C, $[ICl_2^-]_T = 4.13 \times 10^{-6}$ M, $[N_2H_5^+]_T = 3.99 \times 10^{-5}$ M, [HCl] = 1.00 M. The first step is the formation of I_2Cl^- (eq 8) and the second step is its decay (eq 9).

Kinetics of the ICl_2^-/ICl Reaction with Excess $N_2H_5^+$. Spectra of the reaction products were taken after mixing (2.25−6.0) × 10^{-6} M $[ICl_2^-]_T$ with (0.025−5.0) × 10^{-3} M $[N_2H_5^+]_T$ in 1.0 M HCl. After the reaction, all the spectra show the characteristic band due to I^- ($\lambda_{max} = 225$ nm, $\epsilon = 14\,380$ M^{-1} cm^{-1})[30] and with no trace of I_2Cl^-, I_2, or I_3^-. The kinetic data obtained from the reaction of ICl with excess $N_2H_5^+$ show multiple steps as seen for the traces at 225 and 250 nm in Figure 2. The kinetic traces at 270, 280, and 292 nm are similar to those seen at 250 nm. Among these kinetic traces, the largest absorbance increase is obtained at 250 nm, indicating that I_2Cl^- ($\lambda_{max} = 248$ nm, $\epsilon = 55\,000$ M^{-1} cm^{-1})[25] is the major species formed initially. Therefore, the increasing absorbance at 250 nm in Figure 2 represents the formation of I_2Cl^- (eq 8) through the rapid reaction of ICl and I^- ($k = 1.1 \times 10^9$ M^{-1} s^{-1}),[22] while the slower decreasing absorbance is the decay of I_2Cl^- (eq 9). The decay of I_2Cl^- is due to its reaction with $N_2H_5^+$ by the path of ICl not I_2. The reaction of I_2 and $N_2H_5^+$ is too slow (0.7 M^{-1} s^{-1})[10] to account for the decay of I_2Cl^-. The kinetic trace at 225 nm in Figure 2, which is close to the λ_{max} of ICl_2^- and I^-, also shows the loss of ICl_2^- (eq 8) followed by the formation of I^- (eq 9).

Reactions of $N_2H_5^+$ with Excess ICl_2^- and IBr_2^-. It is clear that the reaction of ICl with I^- causes difficulties for the kinetic studies when using excess $N_2H_5^+$. The same problem is expected for the reaction of IBr with excess $N_2H_5^+$. However, these problems can be avoided by using ICl_2^- or IBr_2^- in excess and $N_2H_5^+$ as the limiting reagent. In this method, the rapid reactions of ICl and IBr with I^- are used as the indicator reactions by following the formation of I_2Cl^- and I_2Br^-, respectively. The formation constants are $[I_2Cl^-]/[ICl][I^-] = 7.3 \times 10^8$ M^{-1} for I_2Cl^-,[22] $[I_2Br^-]/[IBr][I^-] = 3 \times 10^6$ M^{-1} for I_2Br^-.[14] The reaction rates of mixtures of ICl_2^- and $N_2H_5^+$ are much faster than the mixtures of I_2Cl^- and $N_2H_5^+$. This is because ICl is the reactive species and its concentration is greatly suppressed by I^- compared to Cl^-. Hence, when ICl_2^-/ICl is used in excess over hydrazine, the reaction in eq 9 is not observed. The same is true for the reaction of excess IBr_2^-/IBr with hydrazine.

The reaction of $N_2H_5^+$ with excess ICl_2^- gives excellent first-order plots monitoring the appearance of I_2Cl^-. The observed first-order rate constants increase proportionally with $[ICl_2^-]_T$ and $[IBr_2^-]_T$, respectively (Figure 3). No saturation effect is observed even at $[ICl_2^-]_T = 21$ mM, which indicates there is

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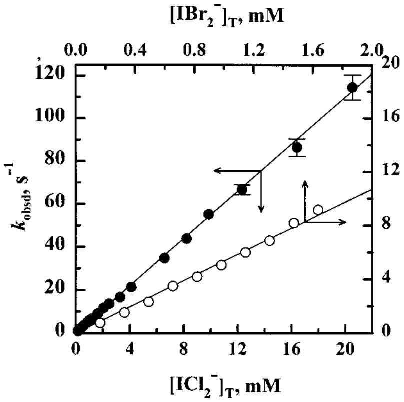

Figure 3. Dependence of the observed first-order rate constants on $[IX_2^-]_T$ for the oxidation of $N_2H_5^+$ with excess IX_2^- at 25.0 °C, $\mu = 1.00$ M. (○) 10^2k_{obsd} vs $[IBr_2^-]_T$, $[Br^-] = 0.491$ M, $[HClO_4] = 0.402$ M, $\lambda = 440$ nm. Result: slope $= 53.6 \pm 0.8$ M^{-1} s^{-1}. (●) k_{obsd} vs $[ICl_2^-]_T$, $[HCl] = 1.00$ M, $\lambda = 275$, 450, and 455 nm. Result: slope $= (5.50 \pm 0.08) \times 10^3$ M^{-1} s^{-1}.

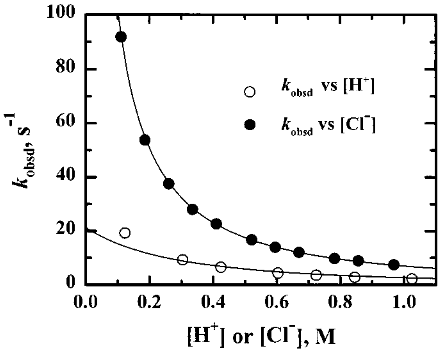

Figure 4. Observed first-order rate constants as a function of $[H^+]$ (○) and $[Cl^-]$ (●) for the oxidation of $N_2H_5^+$ with excess ICl_2^- at 25.0 °C, $\mu = 1.00$ M. Conditions: (○) $[ICl_2^-]_T = 4.14 \times 10^{-4}$ M, $[Cl^-] = 1.025$ M, $\lambda = 275$ nm. (●) $[ICl_2^-]_T = 3.975 \times 10^{-4}$ M, $[HClO_4] = 0.410$ M, $\lambda = 265$ nm. Results: $k_1 = (4.12 \pm 0.07) \times 10^6$ M^{-1} s^{-1} and $k_{-1}/k_2 = 1.9 \pm 0.2$ M^{-2}.

no appreciable concentration of an $ICl{\cdot}N_2H_5^+$ adduct. Although Radhakrishnamurty and co-workers[31] reported a saturation effect at $[N_2H_4]_T = 5.0-50.0$ mM in 0.9 M H^+ for the reaction of I_2 and hydrazine with a complex formation constant of 2.3×10^9 M^{-1}, this result is unreasonable. Recent measurement of the $I_2N_2H_4$ association constant gave a value of 2.0×10^4 M^{-1}, while $N_2H_5^+$ association with I_2 could not be detected.[10] The relative Lewis acid strength of halogens and interhalogens has been assigned as $ICl \gg BrCl > IBr \gg I_2 > Br_2 \gg Cl_2$.[32] If $ICl-N_2H_5^+$ complex formation cannot be observed, the formation of other halogen and interhalogen complexes with $N_2H_5^+$ is highly unlikely.

Proposed Mechanism for the Reaction of $N_2H_5^+$ with Excess ICl_2^- and IBr_2^-. The kinetic observations show that the rates are first-order both in $[IX_2^-]_T$ (Figure 3) and $[N_2H_5^+]_T$ and are suppressed by X^- and H^+ (Figures 4 and 5) (X = Cl, Br). As the Cl^- and Br^- concentrations increase, more ICl and IBr are converted to the unreactive species of ICl_2^- and IBr_2^-, respectively. However, the experimentally observed suppressions by Cl^- and Br^- are greater than can be attributed to this effect. Similarly, as the H^+ concentration increases, more $N_2H_5^+$ is converted to the unreactive $N_2H_6^{2+}$ species, but the H^+ suppression is greater than can be attributed to this effect. A general mechanism is proposed in eqs 10−17 for the reactions

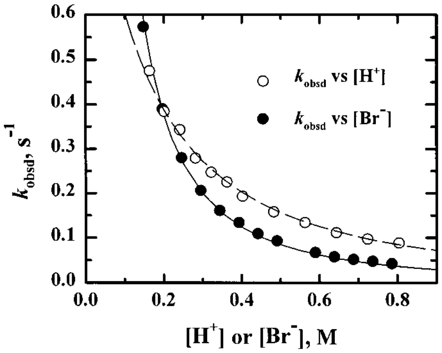

Figure 5. Observed first-order rate constants as a function of $[H^+]$ (○) and $[Br^-]$ (●) for the oxidation of $N_2H_5^+$ with excess IBr_2^- at 25.0 °C, $\mu = 1.00$ M. Conditions: (○) $[IBr_2^-]_T = 8.325 \times 10^{-4}$ M, $[Br^-] = 0.1964$ M, $\lambda = 440$ nm. (●) $[IBr_2^-]_T = 8.34 \times 10^{-4}$ M, $[HClO_4] = 0.201$ M, $\lambda = 440$ nm. Results: $k_1 = (7.6 \pm 0.3) \times 10^4$ M^{-1} s^{-1} and $k_{-1}/k_2 = 28 \pm 2$ M^{-2}.

$$IX + X^- \underset{}{\overset{K_{IX_2}}{\rightleftharpoons}} IX_2^- \qquad \text{fast} \tag{10}$$

$$N_2H_5^+ + H^+ \overset{K_{P2}}{\rightleftharpoons} N_2H_6^{2+} \qquad \text{fast} \tag{11}$$

$$N_2H_5^+ + IX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} IN_2H_4^+ + X^- + H^+ \tag{12}$$

$$IN_2H_4^+ \xrightarrow{k_2} N_2H_3^+ + H^+ + I^- \tag{13}$$

$$N_2H_3^+ \rightleftharpoons N_2H_2 + H^+ \qquad \text{fast} \tag{14}$$

$$IX + N_2H_2 \rightarrow N_2 + I^- + X^- + 2H^+ \qquad \text{fast} \tag{15}$$

$$IX + I^- \overset{K_{I_2X}}{\rightleftharpoons} I_2X^- \qquad \text{fast} \tag{16}$$

$$I_2X^- \overset{K_3}{\rightleftharpoons} I_2 + X^- \qquad \text{fast} \tag{17}$$

of $N_2H_5^+$ and IX (X = Cl, Br). In the first step of the reaction, $N_2H_5^+$ and IX react to form a steady-state intermediate $IN_2H_4^+$ that reacts reversibly with H^+ and X^- (eq 12) or can eliminate I^- and H^+ to form $N_2H_3^+$ (eq 13). The reversible reaction in eq 12 takes into account the additional suppression found for X^- and H^+ concentrations. Subsequent reactions (eqs 14−17) after the rate-determining steps (eqs 12 and 13) are given to show how the known products (N_2, I_2X^-, and I_2) can be formed. The dissociation constant of $N_2H_3^+$ to form diazine (eq 14), N_2H_2, was calculated to be 32 M.[33] We propose diazine as an intermediate, but it is not detected. It must react very rapidly with IX. In excess IX_2^-, there will not be enough N_2H_2 for its dismutation (2.2×10^4 M^{-1} s^{-1})[34] to contribute to the mechanism.

The progress of the reactions is measured by I_2X^- formation, where I_2X^- is in rapid equilibrium with I_2 and X^- (eq 17, $K_3 = 0.6$ M for X = Cl,[25] $K_3 = 0.079$ M for X = Br[35]). The rate expression in eq 18 can be derived from this mechanism, in which $[N_2H_5^+]_T = [N_2H_5^+] + [N_2H_6^{2+}]$ and $[IX_2^-]_T = [IX] +$

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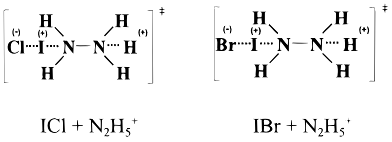
Table 1. Rate Constants for the Oxidations of $N_2H_5^+$ by I_2, IBr, and ICl at 25.0 °C and Complex Formation Constants (K_C) with Pyridine and 3-Methylpyridine

constants	I_2	IBr	ICl
k_1, $M^{-1}\ s^{-1}$	0.7 ± 0.2^a	$(7.6 \pm 0.3) \times 10^{4\ b}$	$(4.12 \pm 0.07) \times 10^{6\ b}$
k_{-1}/k_2, M^{-2}	$(1.2 \pm 0.1) \times 10^{2\ a}$	$28 \pm 2^{\ b}$	1.9 ± 0.2^b
K_C, M^{-1} (py)^c	77	1.24×10^4	2.30×10^5
K_C, M^{-1} (3-MePy)^c	146	1.99×10^4	3.78×10^5

[a] Reference 10, $\mu = 0.50$ M. [b] This work, $\mu = 1.00$ M. [c] In CCl_4, 30 °C; Aloisi, G. G.; Beggiato, G.; Mazzucato, U. *J. Chem. Soc. Trans. Faraday* **1970**, *66*, 3075−3080.

Scheme 1. Transition State for the k_1/k_{-1} Steps



$[IX_2^-]$ (X = Cl, Br). The observed first-order rate constant is defined in eq 19.

$$-\frac{d[N_2H_5^+]_T}{dt} = \frac{k_1k_2[N_2H_5^+]_T[IX_2^-]_T}{(k_2 + k_{-1}[X^-][H^+])(1 + K_{P2}[H^+])(1 + K_{IX_2}[X^-])} \qquad (18)$$

$$k_{obsd} = \frac{k_1[IX_2^-]_T}{\left(1 + \frac{k_{-1}}{k_2}[X^-][H^+]\right)(1 + K_{P2}[H^+])(1 + K_{IX_2}[X^-])} \qquad (19)$$

Experimentally, the k_{obsd} values are decreased by X^- and H^+ concentrations to a greater degree than expected from the equilibria in eqs 10 and 11. This is attributed to the reverse reaction in eq 12 and is expressed by the $\{1 + (k_{-1}/k_2)[X^-][H^+]\}$ term in the denominator of eq 19. Values of the observed first-order rate constants, k_{obsd}, fit eq 19 as $[H^+]$ and $[X^-]$ change (Figures 4 and 5). For the $N_2H_5^+$/ICl reaction, the results give $k_1 = (4.12 \pm 0.07) \times 10^6\ M^{-1}\ s^{-1}$ and $k_{-1}/k_2 = 1.9 \pm 0.2\ M^{-2}$ by using $K_{P2} = 1.72\ M^{-1}$ and $K_{ICl_2} = 76.9\ M^{-1}$ (Figure 4). For the $N_2H_5^+$/IBr reaction, the results give $k_1 = (7.6 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$ and $k_{-1}/k_2 = 28 \pm 2\ M^{-2}$ by using $K_{P2} = 1.72\ M^{-1}$ and $K_{IBr_2} = 285\ M^{-1}$ (Figure 5). Therefore, the proposed mechanism (eqs 10−17) for the reaction of $N_2H_5^+$ with excess ICl_2^- and IBr_2^- is supported by the $[H^+]$, $[Cl^-]$, $[Br^-]$, $[ICl_2^-]_T$, and $[IBr_2^-]_T$ dependence studies.

The proposed transition state for the formation of $IN_2H_4^+$ is shown in Scheme 1, where I^+ is transferred from IX to $N_2H_5^+$ as X^- and H^+ are released. The rate-contributing step in eq 13 is the breakup of $IN_2H_4^+$ to release H^+ and I^-. As a consequence of I^+ transfer and I^- loss, a two-electron oxidation of hydrazine occurs to give diazine, N_2H_2. Another two-electron oxidation is proposed for the rapid reaction of ICl with N_2H_2 to give N_2 and I^- (eq 15).

Relative Reactivities for the Oxidation of Hydrazine. The k_1 rate constants for the first step in the oxidation of $N_2H_5^+$ by I_2, IBr, and ICl are summarized in Table 1. We propose that all three reactions proceed by the I^+ transfer from IX (X = I, Br, Cl) to $N_2H_5^+$. An electron-transfer mechanism has been ruled out for the oxidation of hydrazine by I_2, from which the calculated rate constants are 9 orders of magnitude smaller than the measured rate constants.[10] The k_1 values indicate that the relative reactivities for the oxidation of $N_2H_5^+$ are in the order ICl ≫ IBr ≫ I_2. This parallels the order of their relative Lewis acid strengths[31] as shown by their complex formation constants (K_C) with pyridine and 3-methylpyridine. A plot of log k_1 vs log K_C is linear with a slope of 2.0 ± 0.2 (Figure 6). This correlation indicates that there is a greater extent of I^+ transfer in the formation of the transition state than in the equilibrium reaction, as expected for a rate-determining heterolytic splitting of the I−X bond. The complex formation constant (K_C) with the same electron donor is the measurement of the Lewis acid strength of IX (X = I, Br, Cl) which reflects the polarity of the I−X bonds. The polarity of IX can be attributed to the difference of electronegativity between iodine and X, since the increasing electronegativity of X (Cl > Br > I) will make the iodine atom more positive. This allows an easier I^+ transfer to nucleophiles, even with a very weak Lewis base such as $N_2H_5^+$. In addition, a decrease in the k_{-1}/k_2 values for the sequence I_2, IBr, ICl contributes to the increase in the observed rate constant (eq 19). The range is much smaller than the range of k_1 values but is significant. The suppression expressed by k_{-1}/k_2 parallels the nucleophilicity order of $I^- > Br^- > Cl^-$,[36] which is the reverse order of the relative preference of the leaving groups. As a consequence, the rate of oxidation of $N_2H_5^+$ by ICl is several orders of magnitude faster than that of IBr, which in turn is many orders of magnitude faster than that of I_2.

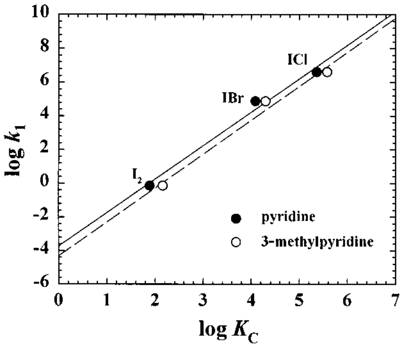


Figure 6. Relationship between log k_1 and log K_C. K_C is the complex formation constant between IX (X = I, Br, Cl) and pyridine or 3-methylpyridine in CCl_4 at 30 °C; slope = 2.0 ± 0.2.

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Supporting Information Available: Tables and figures of spectroscopic and kinetic data (10 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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