Kinetics and Mechanisms of the Oxidation of Hydrazinium Ion ($N_2H_5^+$) by Aqueous Br_2, Cl_2, and BrCl. Electrophilicity Scale for Halogens and Interhalogens

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Very rapid oxidations of $N_2H_5^+$ by Br_2, Cl_2, and BrCl are measured by stopped−flow and pulsed−accelerated-flow methods in acidic solutions with excess $N_2H_5^+$. Second-order rate constants (M^{-1} s^{-1}) at 25.0 °C, $\mu = 1.0$ M are 1.49×10^7, 1.01×10^8, and 5.6×10^8 for the reactions with Br_2, Cl_2, and BrCl, respectively. The reactions are postulated to proceed by nucleophilic reaction of $N_2H_5^+$ with XY electrophiles (XY = Br_2, Cl_2, BrCl) to form $XN_2H_4^+$ with Y^- and H^+ release in the rate-determining step. In the subsequent reactions, we propose that $XN_2H_4^+$ eliminates X^- and H^+ rapidly to form $N_2H_3^+$ and diazine, N_2H_2, which is oxidized by a second Br_2, Cl_2, or BrCl to form N_2 in fast steps. The stoichiometries are measured and confirmed to be 1:2 for the Cl_2 and BrCl reactions. The relative reactivities for the oxidation of $N_2H_5^+$ by halogens and interhalogens (BrCl > Cl_2 > Br_2 > ICl ≫ IBr ≫ I_2) are used to establish an electrophilicity scale (E_{XY}) for this type of reaction in aqueous solution.

Introduction

Hydrazine is a very reactive reducing agent that is used in a variety of applications such as rocket propellants, explosives, boiler feedwater deoxygenation, and pharmaceutical synthesis.[1] The oxidation of hydrazine in aqueous solution was recently reviewed by Stanbury.[2] A general mechanism for the oxidation of hydrazine was given by Higginson[3] in 1957 based on Kirk and Browne's classification[4] of one- and two-electron oxidations. In one-electron oxidations, N_2H_3 was proposed as an intermediate that yields a mixture of hydrazoic acid (HN_3), dinitrogen, and ammonia. In two-electron oxidations, N_2H_2 was proposed as an intermediate that leads to N_2 formation. Iodine is a two-electron oxidant, and the stoichiometry of I_2 with N_2H_4 has been shown to be 2:1.[5] The stoichiometry of the reaction between Cl_2 and N_2H_4 was often assumed to be 2:1.[6] Olson[7] determined that the number of gram atoms of Cl consumed per mole of hydrazine was 4.15 (no precision was given). A stoichiometric reaction

$$N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl \qquad (1)$$

in eq 1 was suggested by Chuprina and co-workers[8] for the removal of chlorine from hydrochloric acid by the use of hydrazine chloride. A similar stoichiometric reaction was used by Kalavska and Rurikova[9] for the determination of hydrazine in its reaction with Br_2. Browne and Shetterly[10] reported that a small amount of hydrazoic acid was formed by the action of chlorine with hydrazine sulfate in both acid and alkaline solutions, but none was formed with iodine reaction. They also detected traces of azide ion (N_3^-) from the reaction of bromine in alkaline solution.

The kinetics of the reactions of hydrazine with aqueous I_2 have been studied by Liu and Margerum.[11] They showed that the reaction between I_2 and N_2H_4 proceeds by the formation of a complex $I_2N_2H_4$. This complex eliminates I^- to form a steady-state species $IN_2H_4^+$, which eliminates I^- and H^+ to form $N_2H_3^+$. The subsequent intermediate, diazine (N_2H_2), is oxidized rapidly by a second I_2 to form N_2. Recently, Jia and Margerum[12] reported that the oxidation of hydrazinium ion ($N_2H_5^+$) by interhalogens ICl and IBr follows a similar mechanism as the $N_2H_5^+/I_2$ reaction. Oxidations of $N_2H_5^+$ by I_2, IBr, and ICl are all proposed to proceed by an I^+ transfer process, and the relative rates are in the order of ICl ≫ IBr ≫ I_2.

Choi and Park[13] attempted to study the reaction between hydrazine and Br_2 in sulfuric acid solutions by a chronopotentiometric method. No consideration was given to the effects of the protonated species of hydrazine, $N_2H_5^+$ and $N_2H_6^{2+}$, or to the Br_3^- complex, and the reported rate constants are not valid. The kinetics and mechanisms of the oxidation of hydrazine by Cl_2 and BrCl have not been previously studied. High acid and halide ion concentrations are needed to suppress the reaction rates and to prevent the hydrolysis of halogens and interhalogens. In high acid concentrations, the reactions are suppressed because $N_2H_5^+$ is less reactive than N_2H_4 while $N_2H_6^{2+}$ is not reactive. The protonation constant of $N_2H_5^+$ to form $N_2H_6^{2+}$, $K_{P2} = [N_2H_6^{2+}]/[N_2H_5^+][H^+]$, is 1.72 M^{-1} at $\mu = 1.0$ M and 25.0 °C.[12] High concentrations of halide ions such as Br^- and Cl^- also suppress the rates because Br_3^-, Cl_3^-, and $BrCl_2^-$ are not reactive. The formation equilibrium constants for these halogen and interhalogen complexes are 16.1 M^{-1} for $K_{Br3} = [Br_3^-]/[Br_2][Br^-]$,[14] 0.18 M^{-1} for $K_{Cl3} = [Cl_3^-]/[Cl_2][Cl^-]$,[14]

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and 3.8 M^{-1} for $K_{BrCl2} = [BrCl_2^-]/[BrCl][Cl^-]$[15] at $\mu = 1.0$ M and 25.0 °C. In this work, rate constants for oxidation of hydrazine by Br_2, Cl_2, and BrCl are measured in high acid and high halide ion concentrations and the corresponding reaction mechanisms are proposed.

Experimental Section

Reagents. Experimental details for the preparation and standardization of solutions and "bromide-free" hydrochloric acid are given in previous work.[12] The ionic strength (μ) was adjusted with aqueous $NaClO_4$ that was recrystallized from water. Stock solution of hypochlorite was prepared by bubbling ultrahigh-purity Cl_2 gas (Matheson, 99.9%) into 0.2 M NaOH solution and stored at 5 °C in a Nalgene bottle. The hypochlorite stock solution was standardized spectrophotometrically at 292 nm ($\epsilon_{OCl} = 362$ M^{-1} cm^{-1}).[16] Chlorine solutions were prepared by T-mixing hypochlorite solution and "Br^--free" hydrochloric acid and used immediately for kinetic studies by transfer from syringes. The bromine solution was prepared by adding liquid Br_2 dropwise to a 0.8 M $HClO_4$ solution to prevent hydrolysis. The concentration of Br_2 was standardized spectrophotometrically at 390 nm ($\epsilon_{Br2} = 175$ M^{-1} cm^{-1}).[14] Solutions of $BrCl_2^-$ were prepared by acidifying a stoichiometric mixture of NaBr and $KBrO_3$ with "Br^--free" HCl:[14]

$$BrO_3^- + 2Br^- + 6H^+ + 6Cl^- \rightarrow 3BrCl_2^- + 3H_2O \qquad (2)$$

The stock solutions of hydrazine were prepared from either $N_2H_4{\cdot}HCl$ or $N_2H_4{\cdot}H_2SO_4$ solids and standardized (in ~5 M HCl) with 0.025 M KIO_3 solution.[17]

Methodology and Instrumentation. Kinetic studies for the reaction of hydrazine and Br_2 were performed on a Applied PhotoPhysics stopped−flow spectrophotometer (APPSF) SX.18MV (optical path length = 0.962 cm), which was controlled from a dedicated Acorn RISC PC (RISC OS 3, version 3.60) with APP software (version 4.33). Kinetic studies for the oxidation of hydrazine by Cl_2 and BrCl were performed on a pulsed−accelerated-flow (PAF) spectrophotometer (model IV).[18] The PAF spectrophotometer uses integrating observation during continuous flow mixing of short duration (0.4 s pulse, optical path length = 2.050 cm). Pseudo-first-order rate constants greater than 10^5 s^{-1} are resolved from the physical mixing processes by variation of flow velocities under turbulent flow conditions.[18] Reactions were followed by the loss of Br_3^- at 266 nm ($\epsilon_{Br3} = 40\,900$ M^{-1} cm^{-1}),[14] Cl_3^- at 230 nm ($\epsilon_{Cl3} = 9400$ M^{-1} cm^{-1}),[14] or $BrCl_2^-$ at 232 nm ($\epsilon_{BrCl2} = 32\,700$ M^{-1} cm^{-1})[14] with excess total hydrazine concentration under pseudo-first-order conditions. The observed pseudo-first-order rate constant is defined in

$$\frac{-d[XY]_T}{dt} = k_{obsd}[XY]_T \qquad (3)$$

where XY = Br_2, Cl_2, and BrCl, and $[XY]_T = [XY] + [XY_2^-]$. Each first-order rate constant, k_{obsd}, measured on the APPSF or PAF is an average of five trials. The k_{obsd} values from the APPSF were corrected for mixing limitations of this instrument by using $k_{corr} = k_{obsd}/[1 - (k_{obsd}/k_{mix})]$, where $k_{mix} = 4.62 \times 10^3$ s^{-1}.[19] All reactions were run at 25.0 ± 0.1 °C and $\mu = 1.0$ M. Spectrophotometric measurements were performed on the Perkin-Elmer Lambda-9 UV/vis/NIR spectrophotometer interfaced to a Zenith 386/20 computer with solutions thermostated to 25.0 ± 0.1 °C.

Results and Discussion

Reaction Stoichiometries. The stoichiometry of the reaction between Cl_2 and $N_2H_5^+$ was determined by mixing a known concentration of excess hydrazine in 1.04 M HCl with known concentrations of hypochlorite solution. The PAF instrument was used as a precise and rapid mixer. This method overcomes the difficulties in quantification and handling of the Cl_2 solutions. When excess hydrazine in 1.04 M HCl is mixed with hypochlorite solution, Cl_2 is generated very quickly from the reaction[20] of HOCl and HCl and reacts rapidly with $N_2H_5^+$. Our preliminary results show that the second-order rate constant for the reaction of $N_2H_5^+$ and HOCl (measured at pH 3.07) is 2.66×10^3 M^{-1} s^{-1}, which is much slower than the corresponding Cl_2 reaction. Three reactions with different concentrations and molar ratios of chlorine and hydrazine were performed on PAF. Approximately 100 mL of solution from 10 pushes was collected for each reaction. The stoichiometry of the reaction between BrCl and $N_2H_5^+$ was determined by mixing a known concentration of excess hydrazine with a known total concentration of BrCl solution in ~6 M HCl, where $BrCl_2^-$ predominates.[15] Data for four reactions with different concentrations and molar ratios of BrCl and hydrazine were obtained. The excess hydrazine in the reaction mixture was back-titrated in ~5 M HCl with 0.01 M KIO_3 standard solution. The average stoichiometries are 2.01 ± 0.03 for the $Cl_2/N_2H_5^+$ reaction and 2.04 ± 0.02 for the $BrCl/N_2H_5^+$ reaction. The results are summarized in Table 1. The precision of our results is no better than 1−2%. Hence, trace levels of other products could be formed. However, if appreciable amounts of N_3^- are formed, it would lead to $XY/N_2H_5^+$ ratios of less than 2.0, and this is not the case. In the Br_2/N_2H_4 reaction, N_3^- was detected only in base,[10] whereas we have strong acid. The $Br_2/N_2H_5^+$ reaction should follow the same stoichiometry as the corresponding Cl_2 and BrCl reactions. The general stoichiometric reaction is described:

$$N_2H_5^+ + 2XY \rightarrow N_2 + 5H^+ + 2X^- + 2Y^- \qquad (4)$$

Reaction of $N_2H_5^+$ and Br_2. With excess total hydrazine ($[N_2H_5^+]_T = [N_2H_5^+] + [N_2H_6^{2+}]$) and high concentrations of Br^- and H^+, the loss of total bromine ($[Br_2]_T = [Br_2] + [Br_3^-]$), observed at 266 nm, follows first-order kinetics. The observed first-order rate constants (measured on the APPSF after the correction for mixing) are first-order in $[N_2H_5^+]_T$ as shown in Figure 1. The observed first-order rate constants decrease with increasing $[H^+]$ and $[Br^-]$ (Figure 2) because of the lack of reactivity of $N_2H_6^{2+}$ and Br_3^-. The data correspond to

$$k_{obsd} = \frac{2k_{Br2}[N_2H_5^+]_T}{(1 + K_{Br3}[Br^-])(1 + K_{P2}[H^+])} \qquad (5)$$

where the $(1 + K_{Br3}[Br^-])$ term corrects for Br_3^- formation and the $(1 + K_{P2}[H^+])$ term corrects for $N_2H_6^{2+}$ formation. The rate suppressions by H^+ and Br^- correspond only to the formation of $N_2H_6^{2+}$ and Br_3^- without any additional H^+ and Br^- suppression (unlike the dependence found for IBr reactions[12]). The resolved second-order rate constant (k_{Br2}) for the reaction of $N_2H_5^+$ and Br_2 is calculated from the slope in Figure 1 in accord with eq 5, which gives a value of $(1.49 \pm 0.02) \times 10^7$ M^{-1} s^{-1} at 25.0 °C and $\mu = 1.0$ M.

Reaction of $N_2H_5^+$ and Cl_2. The oxidation of hydrazine by aqueous chlorine is very fast, and rate suppression due to the

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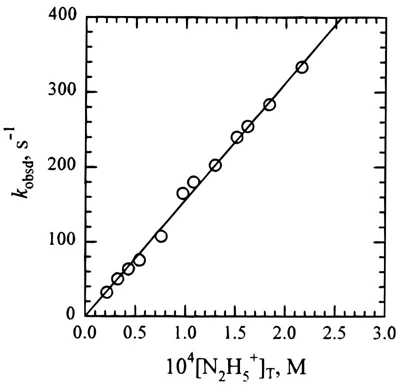


Figure 1. Dependence of the observed first-order rate constants on $[N_2H_5^+]_T$ for the oxidation of $N_2H_5^+$ by Br_2 at 25.0 °C and $\mu = 1.0$ M on the APPSF. Conditions are the following: $[Br_2]_T = (0.37 \text{ to } 1.9) \times 10^{-5}$ M, $[H^+] = 0.246$ M, $[Br^-] = 0.7716$ M, $\lambda = 266$ nm, slope $= (1.56 \pm 0.02) \times 10^6$ M^{-1} s^{-1}.

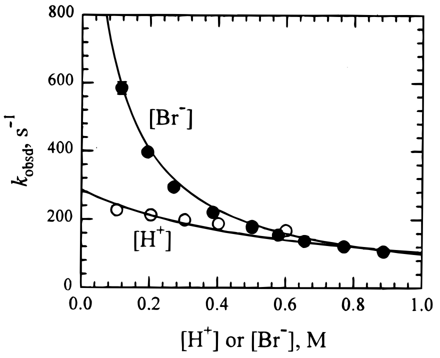


Figure 2. Observed first-order rate constants as a function of $[H^+]$ (○) and $[Br^-]$ (●) for the oxidation of $N_2H_5^+$ by Br_2 at 25.0 °C and $\mu = 1.0$ M on the APPSF: (○) $[N_2H_5^+]_T = 7.63 \times 10^{-5}$ M, $[Br_2]_T = 1.20 \times 10^{-5}$ M, $[Br^-] = 0.3585$ M, $\lambda = 266$ nm; (●) $[N_2H_5^+]_T = 7.63 \times 10^{-5}$ M, $[Br_2]_T = 1.14 \times 10^{-5}$ M, $[H^+] = 0.125$ M, $\lambda = 266$ nm.

Table 1. Measurements of Stoichiometry for the $Cl_2/N_2H_5^+$ and the $BrCl/N_2H_5^+$ Reactions

reaction	$[N_2H_5^+]_T$ M	$[Cl_2]_T$ or $[BrCl]_T$ M	$[N_2H_5^+]_T$ M, unreacted	stoichiometry Cl_2 (or $BrCl)/N_2H_5^+$
$Cl_2 + N_2H_5^+$	0.009 94	0.005 49	0.007 16	1.97 ± 0.02
	0.014 91	0.010 98	0.009 54	2.04 ± 0.01
	0.019 88	0.016 47	0.011 70	2.01 ± 0.01
			ave:	2.01 ± 0.03
$BrCl + N_2H_5^+$	0.009 85	0.011 25	0.004 535	2.06 ± 0.01
	0.012 48	0.009 375	0.007 838	2.02 ± 0.01
	0.017 11	0.010 71	0.011 88	2.05 ± 0.01
	0.018 63	0.007 000	0.015 21	2.05 ± 0.01
			ave:	2.04 ± 0.02

formation of Cl_3^- is small because K_{Cl3} is only 0.18 M^{-1}:

$$Cl_2 + Cl^- \overset{K_{Cl3}}{\rightleftharpoons} Cl_3^- \tag{6}$$

Because of the small fraction of Cl_3^-, high concentrations of total chlorine solution are needed to reach reasonable absorbance. The reactions were studied by the PAF technique under both second-order unequal concentration conditions and pseudo-first-order conditions. In the second-order unequal concentration reactions, the initial total concentration of chlorine was calculated from the initial absorbance of chlorine solution and the calibration curve on PAF under the same conditions.

Table 2. Reactions of $N_2H_5^+$ and Cl_2 under Second-Order Unequal Concentration Conditions on the PAF[a]

$10^4[N_2H_5^+]_T$ M	$10^4[Cl_2]_T$ M	$[N_2H_5^+]_T/[Cl_2]_T$	$10^{-7}k_r$ M^{-1} s^{-1}
2.08	1.45	1.43	6.3 ± 0.1
2.77	2.00	1.39	7.1 ± 0.1
4.16	2.56	1.63	6.11 ± 0.08
5.54	3.12	1.78	6.9 ± 0.2
5.54	1.45	3.82	5.9 ± 0.4
6.93	2.00	3.47	6.5 ± 0.2
8.31	3.12	2.66	7.2 ± 0.2
8.31	2.56	3.25	7.5 ± 0.4
			ave: 6.9 ± 0.5

[a] Conditions: [HCl] = 1.00 M, 25.0 °C, $\lambda = 230$ nm.

Bromide ion can interfere with the reaction of chlorine and hydrazine by forming BrCl and $BrCl_2^-$,[13]

$$Cl_2 + Br^- \rightleftharpoons BrCl_2^- \tag{7}$$

$$BrCl + Cl^- \overset{K_{BrCl2}}{\rightleftharpoons} BrCl_2^- \tag{8}$$

and BrCl is very reactive toward $N_2H_5^+$. The formation equilibrium constant of $BrCl_2^-$ from the reaction of Cl_2 and Br^- (eq 7) is calculated to be 1.2×10^7 M^{-1} by using related equilibrium constants[14] and $E°$ values of Cl_2/Cl^- and Br_2/Br^-. Most of the Br^- (1.0×10^{-5} M) in 1.0 M HCl (without purification) will be converted by Cl_2 to BrCl and $BrCl_2^-$, and its concentration can be as much as 10% of the chlorine solution that is used. Bromide formed from the reaction of BrCl and $N_2H_5^+$ will regenerate BrCl from its reaction with Cl_2 (eq 7). To obtain accurate kinetic measurements, "Br^--free" HCl is used for the reaction of $N_2H_5^+$ and Cl_2.

Rate constants were measured (Table 2) by the PAF technique for a series of reactions under second-order unequal concentration conditions with different $[N_2H_5^+]_T/[Cl_2]_T$ molar ratios in 1.00 M HCl. The resolved second-order rate constant, k_{Cl2}, is calculated from

$$k_{Cl2} = \frac{k_r(1 + K_{Cl3}[Cl^-])(1 + K_{P2}[H^+])}{2} \tag{9}$$

in which k_r is the observed second-order rate constant, $K_{Cl3} = 0.18$ M^{-1}, $K_{P2} = 1.72$ M^{-1}, and [HCl] = 1.00 M. For the reaction of $N_2H_5^+$ and Cl_2, the average second-order rate constant k_{Cl2} is $(1.11 \pm 0.08) \times 10^8$ M^{-1} s^{-1} at 25.0 °C and $\mu = 1.00$ M.

The reactions of $N_2H_5^+$ and Cl_2 under pseudo-first-order conditions were studied with increasing total hydrazine concentrations in 1.00 M HCl. The observed pseudo-first-order rate constants are first-order in total hydrazine concentrations (Figure 3), where the slope k_r is $(6.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1} for the reaction of $N_2H_5^+$ and Cl_2. The resolved second-order rate constant k_{Cl2} is calculated to be $(1.01 \pm 0.03) \times 10^8$ M^{-1} s^{-1} at 25.0 °C and $\mu = 1.00$ M. This second-order rate constant (obtained under the pseudo-first-order conditions) is in good agreement with the rate constant obtained under second-order unequal concentration conditions.

Reaction of $N_2H_5^+$ and BrCl. The plot of the observed first-order rate constants, k_{obsd}, vs $[N_2H_5^+]_T$ is linear as shown in Figure 3. The observed second-order rate constant k_r is the slope in Figure 3, which is $(8.6 \pm 0.8) \times 10^7$ M^{-1} s^{-1} for the reaction of $N_2H_5^+$ and BrCl in 1.00 M HCl. The resolved second-order rate constant, k_{BrCl}, is calculated to be $(5.6 \pm 0.5) \times 10^8$ M^{-1} s^{-1} at 25.0 °C and $\mu = 1.00$ M according to eq 9, where K_{BrCl2}

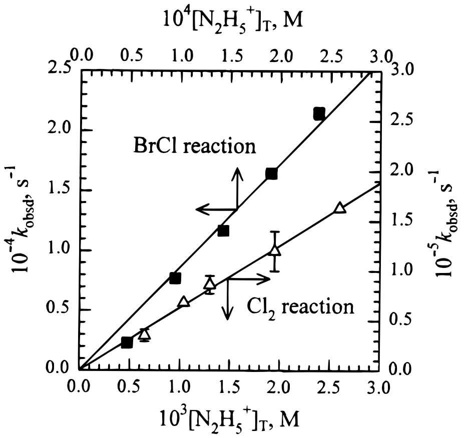
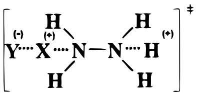


Figure 3. Dependence of the observed first-order rate constants on $[N_2H_5^+]_T$ for the oxidation of $N_2H_5^+$ by Cl_2 (△) and BrCl (■) at 25.0 °C and $\mu = 1.00$ M on the PAF: (△) $10^{-5}k_{obsd}$ vs $10^3[N_2H_5^+]_T$, $[Cl_2]_T = (0.51 \text{ to } 3.30) \times 10^{-4}$ M, [HCl] = 1.00 M, $\lambda = 230$ nm, slope = $(6.3 \pm 0.2) \times 10^7$ M^{-1} s^{-1}; (■) $10^{-4}k_{obsd}$ vs $10^4[N_2H_5^+]_T$, $[BrCl]_T = (0.469 \text{ to } 2.344) \times 10^{-5}$ M, [HCl] = 1.00 M, $\lambda = 232$ nm, slope = $(8.6 \pm 0.8) \times 10^7$ M^{-1} s^{-1}.

Scheme 1. Transition State for the Reactions of $N_2H_5^+$ and XY in Eq 13, Where XY = Br_2, Cl_2, and BrCl



= 3.8 M^{-1} is used instead of K_{Cl3}. The observed first-order rate constants change as a function of $[H^+]$ (from 0.423 to 0.844 M) and $[Cl^-]$ (from 0.462 to 0.928 M), consistent with

$$k_{obsd} = \frac{2k_{BrCl}[N_2H_5^+]_T}{(1 + K_{BrCl2}[Cl^-])(1 + K_{P2}[H^+])} \qquad (10)$$

The decrease of the first-order rate constants with increasing $[H^+]$ and $[Cl^-]$ is due to the formation of $N_2H_6^{2+}$ and $BrCl_2^-$ (eq 8). The terms $(1 + K_{P2}[H^+])$ and $(1 + K_{BrCl2}[Cl^-])$ in eq 10 are used for that correction.

General Mechanism for the Oxidation of $N_2H_5^+$ by XY. From the kinetic studies, a general mechanism for the oxidation of $N_2H_5^+$ by XY is proposed in eqs 11−16, where XY = Br_2, Cl_2, and BrCl. The $N_2H_5^+$ ion acts as a weak nucleophile in the reaction with XY electrophiles to form a reactive intermediate, $XN_2H_4^+$, in the rate-determining step (eq 13). The transition state for reaction 13 is shown in Scheme 1, where the reaction proceeds by concerted X−Y bond cleavage and X−N bond formation with X^+ transfer as a net result. An electron-transfer mechanism has been ruled out for the oxidation of hydrazine by I_2, where the calculated rate constants are 9 orders of magnitude smaller than the measured ones.[11] In the oxidation of $N_2H_5^+$ by ICl and IBr,[12] the first step to form $IN_2H_4^+$ is reversible. However, for Br_2, Cl_2, and BrCl the reverse reaction in eq 13 is not appreciable, and hence, no additional H^+, Br^-, or Cl^- suppressions are observed. The reactive intermediates $BrN_2H_4^+$ and $ClN_2H_4^+$ are more acidic than $IN_2H_4^+$ because bromine and chlorine are more electronegative than iodine, which tends to make eq 13 irreversible. In the subsequent rapid reactions, $XN_2H_4^+$ can eliminate X^- and H^+ to form $N_2H_3^+$ (eq 14), which is in rapid equilibrium with diazine, N_2H_2 (eq 15). The dissociation constant of $N_2H_3^+$ to form N_2H_2 (eq 15) was calculated to be 32 M.[21] We propose diazine as an intermediate, but it is not detected. Finally, diazine is oxidized rapidly by a second XY to form N_2 in multiple steps (eq 16). Therefore, the stoichiometric ratio value of 2 in eqs 5, 9, and 10 is taken into account for the consumption of the second XY.

Table 3. Rate Constants (k_{XY}) of Oxidation of $N_2H_5^+$ by XY at 25.0 °C and Electrophilicities (E_{XY})

XY	k_{XY} M^{-1} s^{-1}	E_{XY} aqueous-phase[d]	E_{XY} gas-phase[e]
I_2	0.70[a]	0	
IBr	7.6×10^4 [b]	5.0	
ICl	4.12×10^6 [b]	6.8	
Br_2	1.49×10^7 [c]	7.3	7.4
Cl_2	1.01×10^8 [c]	8.2	5.1
BrCl	5.6×10^8 [c]	8.9	9.0
ClF			9.8

[a] Reference 11, $\mu = 0.5$ M. [b] Reference 12, $\mu = 1.0$ M. [c] This work, $\mu = 1.0$ M. [d] This work. [e] Reference 25.

$$N_2H_5^+ + H^+ \xrightleftharpoons{K_{P2}} N_2H_6^{2+} \qquad \text{(fast)} \qquad (11)$$

$$XY + Y^- \xrightleftharpoons{K_{XY2}} XY_2^- \qquad \text{(fast)} \qquad (12)$$

$$N_2H_5^+ + XY \xrightarrow{k_{XY}} XN_2H_4^+ + Y^- + H^+ \qquad \text{(rds)} \quad (13)$$

$$XN_2H_4^+ \rightarrow N_2H_3^+ + X^- + H^+ \qquad \text{(fast)} \qquad (14)$$

$$N_2H_3^+ \rightleftarrows N_2H_2 + H^+ \qquad \text{(fast)} \qquad (15)$$

$$N_2H_2 + XY \rightarrow N_2 + 2H^+ + X^- + Y^- \qquad \text{(fast)} \quad (16)$$

Relative Reactivities for the Oxidation of $N_2H_5^+$. Second-order rate constants for the oxidation of $N_2H_5^+$ by halogens and interhalogens are summarized in Table 3. The relative reactivities for the oxidation of $N_2H_5^+$ are in the order of BrCl > Cl_2 > Br_2 > ICl ≫ IBr ≫ I_2. The reactions occur by X^+ (X = I, Br, Cl) transfer rather than electron transfer. A linear free energy relationship was reported[12] for log k_{IX} (X = I, Br, Cl) vs log K_C, where K_C values are the complex formation constants of IX with pyridine and 3-methylpyridine. Halogens and interhalogens can be classified as Lewis acids with decreasing acid strength as ICl ≫ BrCl > IBr ≫ I_2 > Br_2 ≫ Cl_2 by the comparison of the free energies of trihalide formation.[22] This is clearly not the dependence we observe. The reactivities of halogens and interhalogens with nucleophiles depend on their electrophilicity. In the present case the energetics of N−X bond formation and Y^- loss are both important. The contribution from Lewis acidity is less important, although it may account for the greater reactivity of BrCl compared to Cl_2.

From the kinetic studies of halogen and interhalogen addition to olefinic compounds in acetic acid solutions, White and Robertson[23] estimated the following relative reactivities, I_2 (1), IBr (3×10^3), ICl (10^5), Br_2 (10^4), and BrCl (4×10^6), which has some similarities to our results except for the order of Br_2 and ICl and the smaller range of reactivities. Our values of the second-order rate constants (k_{XY}) for the $XY/N_2H_5^+$ reactions range over 9 orders of magnitude and involve Y^- release in aqueous solutions. It is possible to establish an electrophilicity scale for halogens and interhalogens (E_{XY}) according to the

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Swain−Scott free energy relationship:[24]

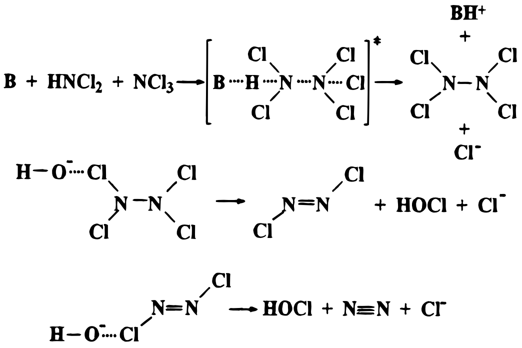
$$\log(k_{XY}/k_{I_2}) = s'E_{XY} \qquad (17)$$

We have selected the second-order rate constant of the $I_2/N_2H_5^+$ reaction (k_{I2}) as a reference and have arbitrarily assigned a value of unity for the sensitivity factor, s'. The resulting electrophilicities of halogens and interhalogens are listed in Table 3. Legon[25] established a limiting gas-phase electrophilicity scale for halogens and interhalogens based on the intermolecular stretching force constants (k_σ) determined from the rotational spectra of prereactive complexes [B···XY]. An empirical equation $k_\sigma = cNE$ was used for calculation, where $c = 0.25$ N m^{-1}, E (electrophilicity) = 10 for HF, and N (nucleophilicity) = 10 for H_2O.[26] Legon's gas-phase electrophilicity scale of XY is a measure of their capacity to interact with a nucleophile B without atom transfer. However, for our reactions in aqueous solution, the halogen cation X^+ transfers to $N_2H_5^+$ as Y^- and H^+ are released. Despite these differences in the nature of the reactions, the gas-phase and aqueous-phase electrophilicities are similar for Br_2 and BrCl but not for Cl_2. The arbitrary choice of k_{I2} as a reference and s' as unity automatically gives an E_{XY} value of zero for I_2, but this is for comparison purposes only and does not mean that it has zero electrophilicity. The fact that $N_2H_5^+$ is a very weak nucleophile permits comparison of the relative rates of the XY electrophiles. A strong nucleophile such as N_2H_4 would react at diffusion-controlled rates with all the XY electrophiles except I_2, where its rate constant is 2.4×10^7 times larger than with $N_2H_5^+$. Our electrophilicity scale of halogens and interhalogens could be used for prediction of the rate constants in their reactions with other weak nucleophiles.

Halohydrazines and Breakpoint Chlorination. In water treatment plants throughout the world, a process known as breakpoint chlorination[27] is used to destroy chloramines and generate dinitrogen. The base-catalyzed reaction of dichloramine with trichloramine is a key pathway for this process, as shown by the proposed mechanism in Scheme 2.[28] When the base (B) is OH^-, the third-order rate constant is 10^8 M^{-2} s^{-1} for the rate expression[28]

$$\frac{d[N_2]}{dt} = k_B[B][HNCl_2][NCl_3] \qquad (18)$$

Scheme 2. Proposed Mechanism for the Base-Catalyzed Reaction of $HNCl_2$ and NCl_3



The decomposition of the proposed intermediates tetrachlorohydrazine and dichlorodiazine are rapid and occur after the rate-determining step, in which N−N bond formation takes place. A question that arises is why the $HNCl_2/NCl_3$ reaction pair carries the bulk of the N_2 generation process. Our present work shows that monochlorohydrazine (eq 14) reacts very rapidly to give diazine, which in turn is rapidly oxidized to N_2. Thus, the replacement of one H by Cl in hydrazine would be sufficient to rapidly generate N_2. In water treatment processes, there are many other reactant pairs such as NH_2Cl/NH_2Cl, $NHCl_2/NHCl_2$, NH_3/NCl_3, NH_2Cl/NCl_3, etc. that might form N−N bonds, where the resulting chlorohydrazine species would rapidly generate N_2. The fact that eq 18 is the preferred path indicates the importance of generating a strong nucleophile (NCl_2^-) that can react with the electrophile (NCl_3) to form an N−N bond and displace Cl^-. The present results also suggest that some of the other reactant pairs could contribute to the breakpoint chlorination process as conditions are altered.

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Supporting Information Available: Listings of kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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