Free Radical Chemistry of Disinfection-Byproducts. 1. Kinetics of Hydrated Electron and Hydroxyl Radical Reactions with Halonitromethanes in Water

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Halonitromethanes are disinfection-byproducts formed during ozonation and chlorine/chloramine treatment of waters that contain bromide ion and natural organic matter. In this study, the chemical kinetics of the free-radical-induced degradations of a series of halonitromethanes were determined. Absolute rate constants for hydroxyl radical, $^{\bullet}OH$, and hydrated electron, e_{aq}^{-}, reaction with both chlorinated and brominated halonitromethanes were measured using the techniques of electron pulse radiolysis and transient absorption spectroscopy. The bimolecular rate constants obtained, k ($M^{-1}\ s^{-1}$), for $e_{aq}^{-}/^{\bullet}OH$, respectively, were the following: chloronitromethane $(3.01 \pm 0.40) \times 10^{10}/(1.94 \pm 0.32) \times 10^{8}$; dichloronitromethane $(3.21 \pm 0.17) \times 10^{10}/(5.12 \pm 0.77) \times 10^{8}$; bromonitromethane $(3.13 \pm 0.06) \times 10^{10}/(8.36 \pm 0.57) \times 10^{7}$; dibromonitromethane $(3.07 \pm 0.40) \times 10^{10}/(4.75 \pm 0.98) \times 10^{8}$; tribromonitromethane $(2.29 \pm 0.39) \times 10^{10}/(3.25 \pm 0.67) \times 10^{8}$; bromochloronitromethane $(2.93 \pm 0.47) \times 10^{10}/(4.2 \pm 1.1) \times 10^{8}$; bromodichloronitromethane $(2.68 \pm 0.13) \times 10^{10}/(1.02 \pm 0.15) \times 10^{8}$; and dibromochloronitromethane $(2.95 \pm 0.43) \times 10^{10} / (1.80 \pm 0.31) \times 10^{8}$ at room temperature and pH ∼7. Comparison data were also obtained for hydroxyl radical reaction with bromoform $(1.50 \pm 0.05) \times 10^{8}$, bromodichloromethane $(7.11 \pm 0.26) \times 10^{7}$, and chlorodibromomethane $(8.31 \pm 0.25) \times 10^{7}\ M^{-1}\ s^{-1}$, respectively. These rate constants are compared to recently obtained data for trichloronitromethane and bromonitromethane, as well as to other established literature data for analogous compounds.

Introduction

One of the major areas of current interest is drinking water quality and, in particular, microbial and pathogen control in potable water. Drinking water is generally disinfected before it enters the water distribution system and ultimately consumed by the general public. Chemicals such as chlorine, ozone, or chloramines, or a combination of these, have typically been used to disinfect water; however, these chemicals can also react with dissolved natural organic matter to form halogenated disinfection-byproducts (DBPs). Many DBPs are suspected to have adverse health affects, and their levels are thus regulated under the Safe Drinking Water Act.[1−4]

One emerging class of DBPs is the halonitromethanes[5] (HNMs, $X_nH_{3-n}CNO_2$, where X = Cl or Br). Halonitromethanes are soluble low molecular weight compounds produced when chlorine[6] and/or ozone[7] are used at drinking water treatment facilities with source waters containing natural organic matter. While trichloronitromethane (chloropicrin) appears to be the most common HNM[8,9] the brominated HNMs, formed in waters also containing natural bromide,[10] are of major concern as they have been shown to be cytotoxic and genotoxic.[7,11]

There is little data available for the lifetime and degradation pathways for HNMs in water; however, one study has shown that trichloronitromethane persists in aqueous environments for at least 240 h in the absence of light.[12] Therefore, if these compounds, upon further toxicity testing, are confirmed to have adverse health effects,[7,11] it is possible that water treatment processes will have to be used to remove them prior to distribution. While a number of treatment alternatives are available for the control of DBPs in treated drinking water, no universally acceptable solution exists. Phase transfer, aeration stripping, or activated charcoal adsorption can be efficient; however, the subsequent disposal of these chemicals still remains a problem. Therefore, there has been a recent shift in philosophy toward alternative approaches that offer complete DBP destruction.[13] One promising group of destructive technologies that has emerged for water treatment are those that generate free radicals in situ, commonly referred to as advanced oxidation technologies (AOTs). AOTs include ozone, ozone in combination with ultraviolet (UV) light or hydrogen peroxide, and hydrogen

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peroxide/UV that generates the oxidizing hydroxyl radical ($^{\bullet}OH$) in water.[14] Some technologies produce both oxidizing and reducing species, such as heterogeneous catalysis using TiO_2/ZnO_2 with UV light (holes and conduction band electrons), sonolysis ($^{\bullet}OH$ radicals and hydrogen atoms, $H^{\bullet}$), or the electron beam irradiation process ($^{\bullet}OH$, $H^{\bullet}$, and hydrated electrons e^{-}_{aq}).

Selection of the most appropriate and cost-effective large-scale DBP removal treatment often relies upon the predictions of computer models.[13] Kinetic computer models give the most information and provide the best test of any proposed treatment[15] as all of the chemistry in the system is considered. A critical component for kinetic modeling of any free radical based technology is a description of the kinetics and mechanisms of the reactions of all the organic compounds involved.

In two recent, radiolysis-based, studies on HNMs, we have determined the kinetics of hydroxyl radical and hydrated electron reaction with bromonitromethane,[16] $(8.36 \pm 0.57) \times 10^7$ and $(3.13 \pm 0.06) \times 10^{10}\ M^{-1}\ s^{-1}$, and trichloronitromethane,[17] $(4.84 \pm 0.42) \times 10^7$ and $(2.13 \pm 0.04) \times 10^{10}\ M^{-1}\ s^{-1}$), respectively. These rate constants demonstrate that the hydrated electron reduction is much faster than the hydroxyl radical oxidation process, as expected. While the reduction process is expected to produce bromide, chloride, and nitrite ions for these two compounds, there is a small but significant difference in the measured rate constants. For hydroxyl radical reaction with bromonitromethane, thermodynamic considerations suggest that reaction would mostly consist of hydrogen atom abstraction to form the carbon-centered radical. This reaction mechanism is not possible for trichloronitromethane, and from product studies and kinetic modeling,[17] it was proposed that most of the hydroxyl radical reaction resulted in nitrite ion formation.

To help establish a global kinetic model of the removal free-radical-based chemistry of all HNMs in water the purpose of this study was to determine the rate constants for the hydrated electron and hydroxyl radical reaction with the other halogenated nitromethanes in water.

Experimental Section

The linear accelerator (LINAC) electron pulse radiolysis system at the Radiation Laboratory, University of Notre Dame was used for all the hydrated electron and hydroxyl radical reaction rate constant determinations. This irradiation and transient absorption detection system has been described in detail elsewhere.[18]

The chemicals used in this study were obtained from Helix Biotech except for trichloronitromethane, bromonitromethane, and the three trihalomethanes (Aldrich Chemical Co.) and were of the highest purity available. All were used as received. Solutions were made with water filtered by a Millipore Milli-Q system, which was constantly illuminated by a Xe arc lamp (172 nm) to keep organic contaminant concentrations below 13 $\mu g\ L^{-1}$ as measured by an on-line TOC analyzer. All solutions were continuously stirred and completely sparged with high-purity N_2O (for hydroxyl radical experiments) or N_2 (hydrated electron or hydrogen atom) to remove dissolved oxygen.

During the irradiation process the solution vessels were bubbled with only the minimum amount of gas necessary to prevent air ingress, to prevent loss of chemical. The solution flow rates in these experiments were adjusted so that each irradiation was performed on a fresh sample. Dosimetry[19] was performed with N_2O-saturated, 1.00×10^{-2} M SCN^- solutions at $\lambda = 475$ nm ($G\epsilon = 5.2 \times 10^{-4}\ m^2\ J^{-1}$) with average doses of 3−5 Gy per 2−3 ns pulse. Throughout this paper, G is defined in $\mu mol\ J^{-1}$, and ϵ is in units of $M^{-1}\ cm^{-1}$.

The hydroxyl radical reaction with HNMs was studied with SCN^- competition kinetics, monitoring the change of absorption intensity of the produced $(SCN)_2^{\bullet -}$ transient at 475 nm. The hydrated electron rate constant was determined by directly following its absorption at 700 nm.

All experiments were performed at ambient temperature (20 ± 0.8 °C) and in unbuffered neutral pH solution.

Results and Discussion

The radiolysis of water produces the free radicals (for the pH range from 3 to 11) in pure water according to the stoichiometry[20,21]

$$H_2O \rightsquigarrow [0.28]^{\bullet}OH + [0.06]^{\bullet}H + [0.27]e_{aq}^{-} + [0.05]H_2 + [0.07]H_2O_2 + [0.27]H_3O^{+} \quad (1)$$

where the yield (G-value) in eq 1 represents the relative number of each species formed. Typical total radical concentrations generated in this study were ∼6−10 μM per pulse.

On the basis of the reaction rate constants measured previously for bromonitromethane[16] and trichloronitromethane,[17] it would be expected that the reductive hydrated electron reaction would dominate all HNM removal from waters. The presence of dissolved oxygen in AOT-treated natural waters containing these chemicals would initially consume any formed reducing hydrated electrons (or hydrogen atoms) to form the superoxide radical; however, for the electron beam AOT the high rate of total delivered dose quickly removes all the dissolved oxygen allowing the subsequent reaction of this reducing species.

The rate constants for hydrated electron reaction with HNMs were determined by fitting exponential decays to the pseudo-first-order kinetics of this species, monitored by its absorption at 700 nm, in pulse-electron irradiated, nitrogen-saturated, solutions at natural pH. These solutions also contained 0.50 M *tert*-butyl alcohol to scavenge the hydroxyl radicals and hydrogen atoms,[20] converting them into relatively inert 2-methyl-2-propanol radicals

$$^{\bullet}OH/H^{\bullet} + (CH_3)_3COH \rightarrow H_2O/H_2 + {}^{\bullet}CH_2(CH_3)_2COH \quad (2)$$

Each kinetic trace was obtained by averaging the data of ∼15 individual pulses, with typical data shown in Figure 1a for chloronitromethane. The decay of this transient was found to be dependent upon the chloronitromethane concentration (Figure 1b), corresponding to a second-order rate constant for the reaction

$$e_{aq}^{-} + ClH_2CNO_2 \rightarrow \text{products} \quad (3)$$

of $k_3 = (3.01 \pm 0.40) \times 10^{10}\ M^{-1}\ s^{-1}$. Similar measurements were performed for the other halonitromethanes of interest in this study, and all values are summarized in Table 1. It is important to note that the errors quoted for all measured rate constants in this work are the combination of the measurement precision and of the initial compound purity.

From the data in Table 1, it is seen that the hydrated electron reduction rate constants for the HNMs are fairly consistent at $\sim 3 \times 10^{10}\ M^{-1}\ s^{-1}$, which can be considered diffusion controlled. No consistent trend with degree or type of halogenation is observed. The two exceptions to this are the fully monohalogenated species, trichloronitromethane and tribromonitromethane, whose rate constants of $(2.13 \pm 0.04) \times 10^{10}$

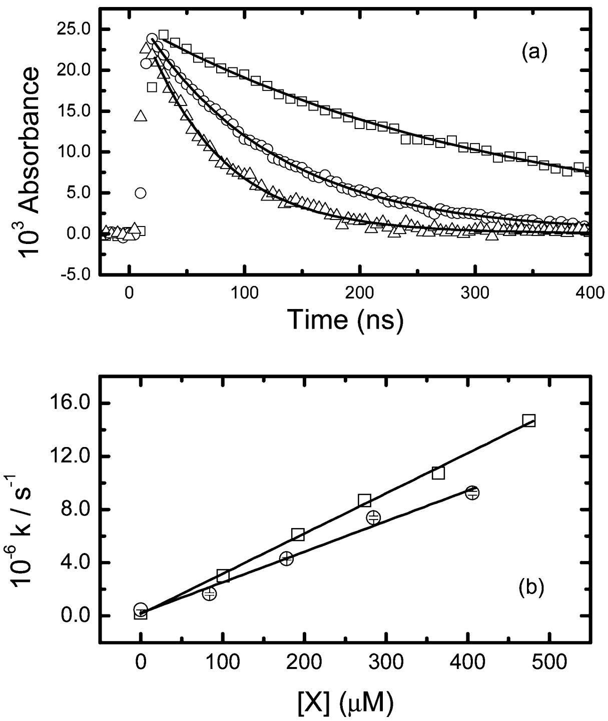

Figure 1. (a) Typical kinetic decay profiles obtained for the hydrated electron absorbance at 700 nm for pulse-electron irradiated aqueous solution at natural pH containing 1.01×10^{-4} (□), 2.74×10^{-4} (○), and 4.75×10^{-4} (△) M chloronitromethane. Curves shown are the average of 10 individual pulses. Solid lines correspond to rate constant fitting with the pseudo-first-order values of 3.00×10^6, 8.67×10^6, and 1.47×10^7 s^{-1}, respectively. (b) Second-order rate constant determination for the reaction of the hydrated electron with chloronitromethane (□) and bromopicrin (○). Single point error bars are one standard deviation, as determined from the average of at least three kinetic traces. The solid line corresponds to weighted linear fits, giving rate constants of 3.01×10^{10} and 2.29×10^{10} M^{-1} s^{-1}, respectively.

M^{-1} s^{-1} [16] and $(2.29 \pm 0.39) \times 10^{10}$ M^{-1} s^{-1}, respectively, are significantly slower than this value (tribronitromomethane data are also shown in Figure 1b).

A search of the literature for analogous reactions (see rate constants listed in Table 1) showed that a decreased rate constant for fully halogenated compounds has also been observed in the hydrated electron reduction of chlorinated ethanes and methanes.[20] However, for both series, there was first a consistent increase in the measured rate constant with the number of chlorine atoms, unlike observed for the halonitromethanes in this study. The change in rate constant for the hydrated electron reaction with chloromethane (1.1×10^9 M^{-1} s^{-1} [22]), dichloromethane (5.45×10^9,[23] 6.3×10^9 M^{-1} s^{-1} [24]), and trichloromethane (1.38×10^{10},[23] 3.0×10^{10} M^{-1} s^{-1} [25]) is fairly linear with the number of chlorine atoms. This rate constant then drops by about 30−50% for hydrated electron reaction with carbon tetrachloride (tabulated values range from 1.3×10^{10} to 2.4×10^{10} M^{-1} s^{-1}).[20] Similarly for the halogenated ethanes,[26] there is a fairly linear rate constant increase of about a factor of 15 when going from chloroethane to pentachloroethane, which is followed by a decrease of 25% for hydrated electron reaction with hexachloroethane.

The analogous literature data for the brominated compounds were much more scattered, with no consistent trends evident. No hydrated electron reaction rate constant for bromomethane or tetrabromomethane was found in the literature, and the value for dibromomethane (2.0×10^{10} M^{-1} s^{-1} [27]) splits the two values reported for tribromomethane (1.0×10^{10},[28] 2.6×10^{10} M^{-1} s^{-1} [23]).

The literature data for the hydrated electron reaction with the mixed halogenated methanes, bromodichloromethane (2.1×10^{10} M^{-1} s^{-1} [23]) and chlorodibromomethane (2.0×10^{10} M^{-1} s^{-1} [23]) suggests that the type of halogen substitution does not significantly affect the rate constant for this process, in agreement with the data that we measured for the HNMs. In addition, the analogous rate constants for nitromethane (2.2×10^{10} M^{-1} s^{-1} [29]) and tetranitromethane (4.6×10^{10} M^{-1} s^{-1} [30]) shows that the nitro group itself significantly activates these compounds, again consistent with the HNM rate constants being faster than the analogous halogenated methanes. Lastly, the one available rate constant for the hydrated electron reaction with trichloroacetonitrile (3.2×10^{10} M^{-1} s^{-1} [31]) is similar to our HNM values, indicating that the cyanide group also activates a substituted methane significantly.

The consistency of the measured rate constants for most of the HNMs suggests a consistent reaction mechanism, indicating that the common nitro group may be significantly involved. At this time, the initial products of hydrated electron reaction are currently being investigated for these HNMs and will be reported in a subsequent publication.

Hydroxyl Radical Rate Constant. The reaction of only hydroxyl radicals was achieved by pre-saturating the solutions with N_2O, which quantitatively converts the hydrated electron, e_{aq}^-, and hydrogen atom to this radical:[20]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + OH^- + {}^{\bullet}OH \qquad k_4 = 9.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \tag{4}$$

$$^{\bullet}H + N_2O \rightarrow {}^{\bullet}OH + N_2 \qquad k_5 = 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \tag{5}$$

The hydroxyl radical reaction with the HNMs did not generate any significant intermediate species absorption in the range 250−800 nm. Therefore, the hydroxyl radical reaction rate constant for HNMs was determined by using SCN$^-$ competition kinetics,[20] based on the competing reactions:

$$^{\bullet}OH + HNM \rightarrow \text{products} \tag{6}$$

$$^{\bullet}OH + SCN^- (+SCN^-) \rightarrow OH^- + (SCN)_2^{\bullet -} \tag{7}$$

and monitoring the $(SCN)_2^{\bullet -}$ absorption at 475 nm. As the HNM reaction transient does not absorb at this wavelength, this hydroxyl radical competition can be analyzed to give the following analytical expression:

$$\frac{[(SCN)_2^{\bullet -}]_o}{[(SCN)_2^{\bullet -}]} = 1 + \frac{k_6[\text{HNM}]}{k_7[\text{SCN}^-]} \tag{8}$$

where $[(SCN)_2^{\bullet -}]_o$ is the final yield of $(SCN)_2^{\bullet -}$ measured for only the blank SCN$^-$ solution, and $[(SCN)_2^{\bullet -}]$ is the reduced yield of this transient when the HNM is present. Therefore a plot of $1/[(SCN)_2^{\bullet -}]$ (or a parameter directly proportional to this intermediate concentration) against the ratio [HNM]/[SCN$^-$] should give a straight line of slope k_6/k_7. On the basis of the established rate constant for hydroxyl radical reaction with SCN$^-$, $k_7 = 1.05 \times 10^{10}$ M^{-1} s^{-1},[20] the k_6 rate constant can then be calculated.

Typical kinetic data obtained at 475 nm are shown in Figure 2a for chloronitromethane. As expected, a decrease in the maximum $(SCN)_2^{\bullet -}$ absorption intensity is observed when the HNM was added. The transformed plot shown in Figure 2b gives a weighted linear fit corresponding to a reaction rate constant of $k = (1.94 \pm 0.32) \times 10^8$ M^{-1} s^{-1}. Comparison plots for

TABLE 1: Determined Rate Constants ($M^{-1}\ s^{-1}$) for Hydroxyl Radical and Hydrated Electron Reaction with Halonitromethanes in Comparison to Analogous Compound Literature Data[a]

		reaction rate constant ($M^{-1}\ s^{-1}$)	
compd	formula	hydrated electron	hydroxyl radical
chloronitromethane	CH_2ClNO_2	**$(3.01 \pm 0.40) \times 10^{10}$**	**$(1.94 \pm 0.32) \times 10^{8}$**
dichloronitromethane	$CHCl_2NO_2$	**$(3.21 \pm 0.17) \times 10^{10}$**	**$(5.12 \pm 0.77) \times 10^{8}$**
trichloronitromethane	CCl_3NO_2	$(2.13 \pm 0.04) \times 10^{10}$ [17]	$(4.84 \pm 0.42) \times 10^{7}$ [17]
bromonitromethane	CH_2BrNO_2	$(3.13 \pm 0.06) \times 10^{10}$ [16]	$(8.36 \pm 0.57) \times 10^{7}$ [16]
dibromonitromethane	$CHBr_2NO_2$	**$(3.07 \pm 0.40) \times 10^{10}$**	**$(4.75 \pm 0.98) \times 10^{8}$**
tribromonitromethane	CBr_3NO_2	**$(2.29 \pm 0.39) \times 10^{10}$**	**$(3.25 \pm 0.67) \times 10^{8}$**
bromochloronitromethane	$CHBrClNO_2$	**$(2.93 \pm 0.47) \times 10^{10}$**	**$(4.2 \pm 1.1) \times 10^{8}$**
bromodichloronitromethane	$CBrCl_2NO_2$	**$(2.68 \pm 0.13) \times 10^{10}$**	**$(1.02 \pm 0.15) \times 10^{8}$**
dibromochloronitromethane	CBr_2ClNO_2	**$(2.95 \pm 0.43) \times 10^{10}$**	**$(1.80 \pm 0.31) \times 10^{8}$**
nitromethane	CH_3NO_2	2.2×10^{10} [29]	
tetranitromethane	$C(NO_2)_4$	4.6×10^{10} [30]	
carbon tetrachloride	CCl_4	$1.3-2.4 \times 10^{10}$ [20]	
trichloromethane	$CHCl_3$	3.0×10^{10} [25] 1.38×10^{10} [23]	$0.7-5.4 \times 10^{7}$ [20]
dichloromethane	CH_2Cl_2	5.45×10^{9} [23] 6.3×10^{9} [24]	9.0×10^{7} [32]
chloromethane	$CHCl_3$	1.1×10^{9} [22]	
tribromomethane	$CHBr_3$	1.0×10^{10} [28]	1.10×10^{8} [28]
			1.3×10^{8} [33]
			$(1.50 \pm 0.05) \times 10^{8}$
		2.6×10^{10} [23]	
dibromomethane	CH_2Br_2	2.0×10^{10} [27]	9.9×10^{7} [33]
bromodichloromethane	$CHBrCl_2$	2.1×10^{10} [23]	**$(7.11 \pm 0.26) \times 10^{7}$**
chlorodibromomethane	$CHBr_2Cl$	2.0×10^{10} [23]	**$(8.31 \pm 0.25) \times 10^{7}$**
trichloroacetonitrile	CCl_3CN	3.2×10^{10} [31]	3.9×10^{7} [31]

[a] Values determined in this study are in bold.

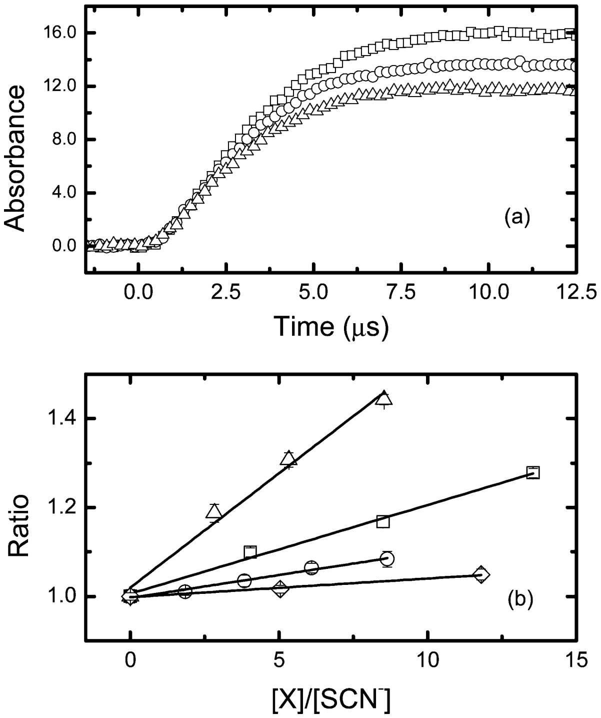

Figure 2. (a) Kinetics of $(SCN)_2^{\bullet-}$ formation at 475 nm for N_2O-saturated 5.27×10^{-5} M SCN^- containing zero (□), 4.49×10^{-4} (○), and 1.02×10^{-3} (△) M chloronitromethane at natural pH and room temperature. (b) Competition kinetics plot for hydroxyl radical reaction with dibromonitromethane (△), chloronitromethane (□), bromodichloronitromethane (○), and bromodichloromethane (◇) (not all data obtained shown) with SCN^- as a standard. Solid lines are weighted linear fits, corresponding to slopes of 0.0452 ± 0.0048, 0.0185 ± 0.0012, 0.0098 ± 0.0012, and 0.00677 ± 0.0002, respectively.

dibromonitromethane and bromodichloronitromethane are also shown in Figure 2b. The calculated rate constants for all the HNMs of this study are given in Table 1, again in comparison to analogous literature data.

The associated error values with these hydroxyl radical rate constants are again the combination of the measurement precision and the initial compound purity. However, for these relatively slow rate constant values, the effects of impurities will be far more important. Consultation with the manufacturer showed that the impurities in our HNMs were only other substituted halonitromethanes, which have comparable (within a factor of 5) hydroxyl radical reactivity. For the HNMs that had an initial purity of less than 99%, but whose impurity constituents reacted at slower rate constants (dichloronitromethane, bromodichloronitromethane, chlorodibromonitromethane, and dibromonitromethane), the measured rate constant is believed to be correct as listed in Table 1, with the corresponding error limits determined mostly by the initial compound purity. However, for chloronitromethane and bromodichloronitromethane, which contained the impurities dichloronitromethane and dibromonitromethane, respectively, it is recognized that the measured rate constants may only be upper-limit values. To accommodate the effects of the more reactive impurities for these latter two compounds, the error limits given in Table 1 were expanded appropriately.

On the basis of these measured rate constants, some qualitative trends are evident for the oxidative hydroxyl radical reaction with the HNMs. The reaction rate constant for chloronitromethane is about a factor of 2 lower than that for dichloronitromethane, $(5.12 \pm 0.77) \times 10^{8}\ M^{-1}\ s^{-1}$, with again a decrease in reaction rate constant for trichloronitromethane, $(4.84 \pm 0.42) \times 10^{7}\ M^{-1}\ s^{-1}$. A similar trend is seen for the brominated HNMs; the rate constant increases from bromonitromethane, $(8.36 \pm 0.57) \times 10^{7}\ M^{-1}\ s^{-1}$, to dibromonitromethane, $(4.75 \pm 0.98) \times 10^{8}\ M^{-1}\ s^{-1}$, with a slight decrease seen for tribromonitromethane, $(3.25 \pm 0.67) \times 10^{8}\ M^{-1}\ s^{-1}$. Unfortunately, there is considerably less literature data available for analogous compounds to make any meaningful comparison. No literature rate constants for the $^{\bullet}OH$ reaction with nitromethane, tetranitromethane, carbon tetrachloride, chloromethane, or bromomethane were found. There is a slight decrease in hydroxyl radical rate constant observed in going from dichloromethane (9.0 × 10^7 M^{-1} s^{-1} [32]) to trichloromethane (values range from 0.7 to 5.4 × 10^7 M^{-1} s^{-1} [20]). However, the corresponding values for dibromomethane (9.9 × 10^7 M^{-1} s^{-1} [33]) and tribromomethane (1.1 × 10^8 M^{-1} s^{-1},[28] 1.3 × 10^8 M^{-1} s^{-1} [33]) show the opposite effect. To confirm this latter trend, we also measured the hydroxyl radical reaction rate constant for tribromomethane in this study, using our thiocyanate competition kinetics methodology. A value of $(1.50 \pm 0.05) \times 10^8$ M^{-1} s^{-1} was obtained, which is slightly higher than the two previous determinations, but confirms the trend that this rate constant is higher than that measured for dibromomethane.

No literature data were found for the mixed chloro−bromo substituted methanes, so rate constants for hydroxyl radical reaction with bromodichloromethane and chlorodibromomethane were also evaluated in this work. Values of $(7.11 \pm 0.26) \times 10^7$ M^{-1} s^{-1} (see Figure 2b for some of the data points obtained) and $(8.31 \pm 0.25) \times 10^7$ M^{-1} s^{-1} were calculated, respectively. These two rate constants show an increase with more bromine atoms present, and again demonstrate that the nitro group in the HNMs slightly activates these molecules.

On the basis of the range of measured rate constants for the HNMs, it is clear that different reaction mechanisms are occurring. Thermodynamic considerations suggest that if the HNM has a hydrogen atom, then its abstraction will be the most likely reaction pathway. Greater substitution by halogen atoms will increase the reactivity of the HNM, making it easier to abstract the remaining hydrogen atoms, which could correspond to faster rate constants. However, there are also steric effects to be considered. Work on the initial products of the hydroxyl radical reaction is currently under investigation.

Conclusion. The measured values for hydrated electron reaction with a series of halonitromethanes show that the reaction rate constants are consistent at ∼3 × 10^{10} M^{-1} s^{-1}, except for the fully substituted trichloronitromethane and tribromonitromethane which are slower, about 2.2 × 10^{10} M^{-1} s^{-1}. The consistency of these data should allow a simple weighted averaging of this dominant reduction value in any kinetic computer model, thereby simplifying the overall coding involved. The oxidizing hydroxyl radical reactions are much slower, and show some qualitative trends with increasing number and type of substitution. These trends are fairly consistent with other data available in the literature for analogous compounds.

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References and Notes

(1) Alvarez, N.; Clark, S.; Schneider, S. *Opflow* **1999**, *25*, 11.

(2) Richardson, S. D.; Thruston, A. D., Jr.; Caughran, T. V.; Chen, P. H.; Collette, T. W.; Floyd, T. L.; Schenck, K. M.; Lykins, B. W., Jr.; Sun, G.-R.; Majetich, G., *Environ. Sci. Technol.* **1999**, *33*, 3378−3383.

(3) Ehlers, L. *WSTB Newslett.* **2000**, *17*, 1−2.

(4) *Fed. Regist*. **1998**, *90*, 69389.

(5) Weinberg, H. S.; Krasner, S. W.; Richardson, S. D.; Thurston, D., Jr. 2002, EPA/600/R-02/068.

(6) Thibaud, H.; De Laat, J.; Dore, M. *Water Res.* **1988**, *22*, 381−390.

(7) Richardson, S. *Anal. Chem.* **2003**, *75*, 2831−2857.

(8) Merlet, N.; Thibaud, H.; Dore, M. *Sci. Total Environ*. **1985**, *47*, 223−228.

(9) Becke, C.; Maier, D.; Sonthheimer, H. *Vom Wasser* **1984**, *62*, 125−135.

(10) Cavenaugh, J. E.; Weinberg, H. S.; Gold, A.; Sangalah, R.; Marbury, D.; Glaze, W. H.; Collette, T. W.; Richardson, S. D.; Thruston, A. D., Jr. *Environ. Sci. Technol*. **1992**, *26*, 1658−1662.

(11) Plewa, M. J.; Wagner, E. D.; Jazwierska, P.; Richardson, S. D.; Chen, P. H.; McKague, A. B. *Environ. Sci. Technol.* **2004**, *38*, 62−68.

(12) Wilhelm, S. N.; Shepler, K.; Lawrence, L. J.; Lee, H. *Environment Fate of Chloropicrin*; Seiber, J. N., Woodrow, J. E., Yates, M. V., Knuteson, J. A., Wolfe, N. L., Yates, S. R., Eds.; ACS Symp. Ser. No. 652, Fumigants Environmental Fate, Exposure, and Analysis; American Chemical Society: Washington, DC, 1996; Chapter 8, pp 80−93.

(13) Bolton, J. R.; Valladares, J. E.; Zanin, J. P.; Cooper, W. J.; Nickelsen, M. G.; Kajdi, D. C.; Waite, T. D.; Kurucz, C. N. *J. Adv. Oxid. Technol*. **1998**, *3*, 174−181.

(14) Adewuyi, Y. G. *Environ. Sci. Technol*. **2005**, *39*, 3409−3420.

(15) Crittenden, J. C.; Hu, S.; Hand, D. W.; Green, S. A. *Water Res.* **1998**, *33*, 2315−2328.

(16) Cole, S. K.; Cooper, W. J.; Mincher, B. J.; Fox, R. V.; Gardinali, P. R.; O'Shea, K. E.; Mezyk, S. P. In *Photocatalytic and Advanced Oxidation Processes for Treatment of Air, Water, Soil and Surfaces*; Ollis, D. F., Al-Ekabi, H., Eds.; Redox Technologies, Inc., 2005; pp 311−317.

(17) Cole, S. K.; Cooper, W. J.; Fox, R. V.; Gardinali, P. R.; Mezyk, S. P.; Mincher, B. J.; O'Shea, K. E. *Environ. Sci. Technol*. Submitted for publication.

(18) Whitman, K.; Lyons, S.; Miller, R.; Nett, D.; Treas, P.; Zante, A.; Fessenden, R. W.; Thomas, M. D.; Wang, Y. *Linear Accelerator For Radiation Chemistry Research at Notre Dame*; In IEEE Proceedings Particle Accelerator Conference and International Conference on High Energy Accelerators, Dallas, Texas, 1995; pp 131−133.

(19) Buxton, G. V.; Stuart, C. R. *J. Chem. Soc., Faraday Trans*. **1995**, *91*, 2, 279−281.

(20) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−886.

(21) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*; John Wiley & Sons: New York, 1964; Chapter 8, pp 237−308.

(22) Balkas, T. I.; Fendler, J. H.; Schuler, R. H. *J. Phys. Chem.* **1970**, *74*, 4497−4505.

(23) Tobien, T.; Cooper, W. J.; Asmus, K.-D. *Natural Organic Matter and Disinfection-By-Products*; Barrett, S., Krasner, S., Amy, G., Eds.; ACS Symposium Series 761; American Chemical Society: Washington, DC, pp 270−281.

(24) Balkas, T. I. *Int. J. Radiat. Phys. Chem.* **1972**, *4*, 199−208.

(25) Hart, E. J.; Gordon, S.; Thomas, J. K. *J. Phys. Chem.* **1964**, *68*, 1271−1274.

(26) Milosavljevic, B. H.; LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A* **2005**, *in press.*

(27) Hayes, D.; Schmidt, K. H.; Meisel, D. *J. Phys. Chem.* **1989**, *93*, 6100−6109.

(28) Lal, M.; Mahal, H. S. *Radiat. Phys. Chem.* **1992**, *40*, 23−26.

(29) Wallace, S. C.; Thomas, J. K. *Radiat. Res*. **1973**, *54*, 49−62.

(30) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1965**, *69*, 53−70.

(31) Lal, M.; Schoeneich, C.; Moenig, J.; Asmus, K.-D. *Int. J. Radiat. Biol.* **1988**, *54*, 773−785.

(32) Getoff, N. *Radiat. Phys. Chem.* **1991**, *37*, 673−680.

(33) Haag, W. R.; Yao, C. C. D. *Environ. Sci. Technol.* **1992**, *26*, 1005−1013.