

# Rate Coefficient Measurements of Hydrated Electrons and Hydroxyl Radicals with Chlorinated Ethanes in Aqueous Solutions

Bratoljub H. Milosavljevic,<sup>†</sup> Jay A. LaVerne,<sup>\*,‡</sup> and Simon M. Pimblott<sup>†,‡</sup>

Radiation Laboratory and Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

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Rate coefficients for the reactions of hydrated electrons and hydroxyl radicals with various chloroethanes were determined in aqueous solutions using pulse radiolysis techniques. The rate coefficients for the hydrated electron increase from  $0.17 \times 10^9$  to  $16.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  with increasing number of chlorine atoms from monochloroethane to hexachloroethane. Very little difference in rates is found between the isomers. Rate coefficients for the OH radicals range from 1 to  $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  and have very little variation with the number of chlorine atoms except when no H atom is available on a carbon atom. The use of competition kinetics with low concentrations of  $\text{SCN}^-$  as a reference is reviewed and suitable model simulations proposed. Possible explanations for the discrepancies between the previously published rate coefficients and the present values are offered.

## Introduction

The radiation chemistry of chloroalkanes in aqueous solutions is important from both fundamental (nonpolar reactants in a polar medium that stabilizes radiolysis products such as  $\text{Cl}^-$ ) and applied (water purification and corrosion) aspects. The deposition of energy by ionizing radiation in dilute solutions is mainly to the water molecules and leads to the production of transient species such as the hydrated electron, hydrogen atom, H, and hydroxyl radical, OH.<sup>1,2</sup> Solute degradation occurs by reactions with these radical species. Knowledge of the rate coefficients for the reactions of the transient water species with the chloroalkanes is required to understand the overall reaction kinetics in aqueous solutions and to predict radiolytic effects using computer model simulations. These models are useful for analyzing radiolytic yields and for elucidating the mechanistic details of long-time corrosion or stability concerns. Chlorinated ethanes were examined in this work because they are representative of typical chlorinated contaminants found in the environment, and the variation in reaction rates with the number of chlorine atoms offers information on the mechanisms involved.

Rate coefficients for the reaction of transient water species with a wide variety of aqueous solutes have been compiled.<sup>3</sup> This compilation includes several rate coefficients for the reactions of the hydrated electron, H atom, or OH radical with different chloroethanes.<sup>4–9</sup> Suitably scaled results from gas-phase studies may also be used to predict aqueous chemistry of the OH radical.<sup>10</sup> However, a complete set of reactions of water products with chloroethanes does not exist. More importantly, rather large discrepancies are observed between the published values. Rate coefficients for the reactions of the hydrated electron are usually determined by directly observing its optical decay using pulse radiolysis techniques.<sup>3</sup> The OH radical is not readily observed optically, and most of its rate coefficients are evaluated by competition kinetics with  $\text{SCN}^-$ .<sup>3</sup>

A typical derivation of the competition kinetics describing the reaction of OH radicals with  $\text{SCN}^-$  and another solute usually involves an extensive simplification of the reaction mechanism for ease of application to the observed data.<sup>11</sup> The  $\text{SCN}^-$  system involves a number of equilibrium steps and oversimplification can lead to erroneous conclusions.<sup>12</sup> Often the rate coefficient can only be obtained by application of a kinetic simulation that models the specific system under examination. The measurement of accurate rate coefficients coupled with an analysis of the values in the literature would greatly aid in the understanding of the radiolysis of aqueous solutions of chloroethanes.

This work presents the results of the pulse radiolysis of aqueous solutions of monochloroethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, and hexachloroethane. Rate coefficients are determined for the reaction of the hydrated electron and OH radical with each of these compounds. The reported values were compared to the previously measured data and possible explanations for the discrepancies are offered. An analysis of the possible errors in the use of competition kinetic techniques is presented.

## Experimental Section

Pulse radiolysis experiments were performed using 2 ns pulses of 8 MeV electrons from the Notre Dame Radiation Laboratory linear accelerator (TB-8/16-1S linac). The linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described in detail elsewhere.<sup>13</sup> All measurements were performed at 20 °C in a high-purity silica cell of 1 cm optical path length. The radiolysis cells were sealed throughout the radiolysis measurement to avoid evaporation of the solute. Samples were replaced often to avoid solute depletion or product buildup. The concentration of radicals generated was approximately  $4.0 \mu\text{M}/\text{pulse}$  with a dose of about 7 Gy (700 rads)/pulse as determined by the thiocyanate dosimeter.

KSCN (Aldrich) was of the highest purity commercially available and was dried in a vacuum prior to use. High-purity

\* Corresponding author. E-mail: laverne.1@nd.edu.

<sup>†</sup> Radiation Laboratory.

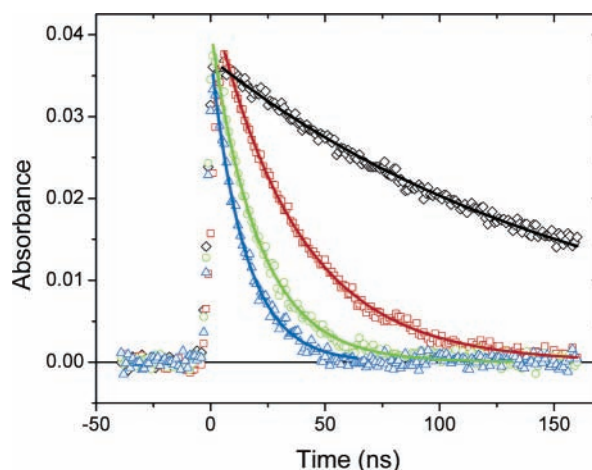
<sup>‡</sup> Department of Physics.

1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, and hexachloroethane chromatographic standards (with no added stabilizer) from Chem-Service were used as received. Gaseous monochloroethane was from Aldrich. Water was purified using an in-house H<sub>2</sub>O only system consisting of a UV lamp and several microporous ultrafilters giving a TOC of a few parts per billion. A kinetic trace of the decay of the hydrated electron in neat water showed no sign of impurities that could interfere in these experiments.

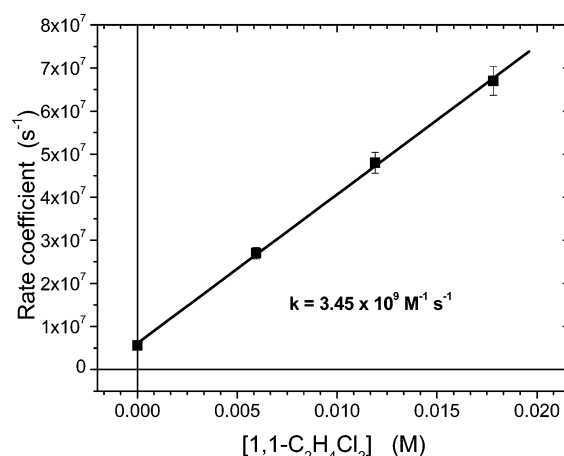
Chloroalkanes are difficult to solubilize in water due to the large differences in polarity. At the same time, they are very volatile and evaporate from ordinary (ground stoppered) volumetric flasks. Great care was taken to maintain a constant, known concentration of the chloroethanes throughout the course of the pulse radiolysis experiments. Considerable information is available on the solubility of the chloroethanes.<sup>14</sup> Solutions of the liquid chloroethanes were made in various concentrations up to the maximum by placing measured volumes of the solute in water. The sample containers consisted of volumetric flasks with vacuum tight stopcocks in place of the normal ground ones. The solutions were stirred vigorously for at least 48 h to completely solubilize the chloroethanes. No significant hydrolysis of chloroethanes was observed in this time period as determined by ion chromatographic measurements of the chloride anion. Samples were then transferred to the radiolysis cell using a gastight syringe and irradiated with electrons from the linac. Monochloroethane was examined in a cell containing a cuvette separated from a 1 L flask by a vacuum stopcock. Water was added and degassed before a known pressure of monochloroethane was added. The water and gas were then vigorously stirred, and the concentration of monochloroethane in the aqueous phase was determined using Henry's law.<sup>14</sup> No variations in results were observed for mixing times from 15 min to 6 h, indicating rapid attainment of equilibrium between the gas phase and the water. Hexachloroethane is a solid and less volatile than the other chloroethanes, but insoluble in water alone. Solutions in water–alcohol mixtures were made by placing a weighed sample into degassed liquids.

To prevent a (mainly unpredictable) decrease in the chloroethane concentration during deoxygenation by bubbling with an inert gas, the rate coefficient measurements were performed with aerated solutions, except for monochloroethane as discussed above. The presence of oxygen can give a small contribution to the hydrated electron decay because the pseudo-first-order rate coefficient for this reaction is about  $5 \times 10^6 \text{ s}^{-1}$  ( $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \times 0.25 \times 10^{-3} \text{ M}$ ).<sup>3</sup> Oxygen competition with the chloroethanes for the hydrated electron was kept to a minimum by adjustment of the solute concentration. The upper detection limit of the pulse radiolysis apparatus is about  $1 \times 10^8 \text{ s}^{-1}$ , which is sufficiently fast to limit contributions due to hydrated electron reaction with oxygen in the time range of the observations.

The concentrations of aqueous solutions of chloroethanes are subject to change due to hydrolysis. Hydrolysis of chloroethanes produces the hydronium ion, H<sub>aq</sub><sup>+</sup>, which readily reacts with the hydrated electron with a rate coefficient equal to  $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>3</sup> Even 10% hydrolysis of a 50 mM 1,1-dichloroethane solution results in a scavenging capacity of  $1.2 \times 10^8 \text{ s}^{-1}$  ( $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \times 5 \text{ mM}$ ) for the hydrated electron by the hydronium ion. The scavenging capacity of 1,1-dichloroethane is only  $1.6 \times 10^8 \text{ s}^{-1}$  ( $3.45 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \times 45 \text{ mM}$ ) resulting in an effective doubling of the observed decay rate of the hydrated electron. Low concentrations of the hydronium ion



**Figure 1.** Decay of the absorbance of the hydrated electron at 700 nm with ( $\diamond$ ) 0.0, ( $\square$ ) 6, ( $\circ$ ) 12, or ( $\triangle$ ) 18 mM of 1,1-dichloroethane. The solid lines are obtained from a simulated model fit to the data.



**Figure 2.** Pseudo-first-order rate coefficients of the hydrated electron decay as a function of 1,1-dichloroethane concentration. The slope of the fitted line gives a second-order rate coefficient of  $3.45 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The intercept is due to the reaction of O<sub>2</sub>.

are important for accurate rate measurements since it readily reacts with the hydrated electron. The Cl<sup>-</sup> concentration was measured using ion chromatography prior to each pulse radiolysis experiment assuming [Cl<sup>-</sup>] = [H<sub>aq</sub><sup>+</sup>]. Only fresh stock solutions were used with [Cl<sup>-</sup>] < 100 μM in all cases.

## Results and Discussion

**Hydrated Electron Reactions.** The hydrated electron has a strong absorption with a maximum at about 720 nm in water at 20 °C.<sup>3</sup> Variation in the decay of the hydrated electron absorption with an added solute offers a simple method for determining the associated rate coefficient. Rate coefficients for hydrated electron reactions were obtained from simple exponential fits to the kinetic traces. Figure 1 shows the decay of the hydrated electron at 720 nm in neat water and with different concentrations of 1,1-dichloroethane. The increase in decay rate with increasing solute concentration is readily apparent.

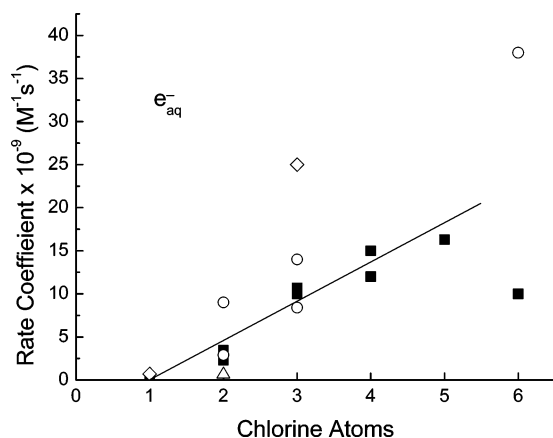
Figure 2 gives a plot of the rate coefficients for the reaction of the hydrated electron with 1,1-dichloroethane as a function of solute concentration. The rate coefficients were obtained from the optimized fits to the decay traces in Figure 1 using both solution methods. The slope of a straight line fit to the data of Figure 2 gives a rate coefficient of  $3.45 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . A similar analysis technique was used for the other chloroethanes,

TABLE 1: Rate Coefficients of Various Chloroethanes with Solvated Electron and Hydroxyl Radical<sup>a</sup>

| compound                           | $e_{\text{sol}}^-$<br>$k \times 10^{-9} (\text{M}^{-1} \text{s}^{-1})$ | OH<br>$k \times 10^{-8} (\text{M}^{-1} \text{s}^{-1})$ | ref        |
|------------------------------------|--|--|------------|
| ethane                             |  | 14.0   | ARI-89 (6) |
| monochloroethane                   | 0.17   | 5.5  | this work  |
|                                    | 0.7  |  | ARI-89 (6) |
| 1,1-dichloroethane                 | 3.45   | 2.35 <sup>b</sup>                                      | CR-85 (10) |
|                                    | 9.0  | 1.3  | this work  |
|                                    |  | 1.3  | IJB-88 (4) |
|                                    |  | 1.57 <sup>b</sup>                                      | CR-85 (10) |
| (solvent: ethanol)                 | 3.1  | —  | this work  |
| 1,2-dichloroethane                 | 2.3  | 2.2  | this work  |
|                                    | 2.9  | 2.0  | IJB-88 (4) |
|                                    | 0.64   | 7.9  | RPC-90 (5) |
|                                    |  | 1.34 <sup>b</sup>                                      | CR-85 (10) |
| (solvent - ethanol)                | 1.92   | —  | this work  |
| 1,1,1-trichloroethane              | 10   | <0.05  | this work  |
|                                    | 14   | 0.40   | IJB-88 (4) |
|                                    | 25   | 1  | ARI-89 (6) |
|                                    |  | 0.09 <sup>b</sup>                                      | CR-85 (10) |
| 1,1,2-trichloroethane              | 10.7   | 3.0  | this work  |
|                                    | 8.4  | 1.1  | IJB-88 (4) |
|                                    |  | 1.3  | EST-92 (9) |
|                                    |  | 1.92 <sup>b</sup>                                      | CR-85 (10) |
| 1,1,1,2-tetrachloroethane          | 15   | 0.1  | this work  |
|                                    |  | 0.18   | JPC-91 (7) |
| 1,1,2,2-tetrachloroethane          | 12   | 2.5  | this work  |
|                                    |  | 1.42 <sup>b</sup>                                      | CR-85 (10) |
| pentachloroethane                  | 16.3   | <0.05  | this work  |
|                                    |  | 1.40 <sup>b</sup>                                      | CR-85 (10) |
| hexachloroethane (50–100% ethanol) | 10.0–11.5  | —  | this work  |
| (methanol)                         | 16.0   |  | this work  |
| (isopropyl alcohol)                | 15.0   |  | this work  |
| (40% <i>tert</i> -butyl alcohol)   | 4.5  |  | this work  |
| (40% <i>tert</i> -butyl alcohol)   | 38.0   |  | IJB-88 (4) |

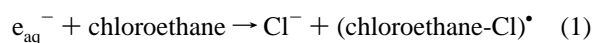
<sup>a</sup> Errors in the present work are less than  $\pm 5\%$ . <sup>b</sup> Density scaled gas-phase data.

and the results are given in Table 1. The intercept of the line in Figure 2 is due to reaction of the hydrated electron with oxygen. It can be seen that the presence of oxygen can be readily accommodated in the determination of the rate coefficient. Removing the oxygen leads to far more serious consequences because of simultaneous evaporation of the chloroethane. The value of the intercept in Figure 2 is  $5.6 \times 10^6 \text{ s}^{-1}$  in good agreement with the literature value for reaction of the hydrated electron with air. The rate coefficients for the reaction of the hydrated electron with the chloroethanes vary from about  $0.17 \times 10^9$  to  $15.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ; see Table 1. Figure 3 shows the hydrated electron rate coefficient as a function of the number of chlorine atoms. No major variation is observed between the



**Figure 3.** Rate coefficients for the hydrated electron reaction with the chloroethanes as a function of chlorine atom content: (■) this work, (○) ref 4, (△) ref 5, and (◇) ref 6. The solid line shows the suggested trend for the lighter chloroethanes.

different isotopes, but the rate coefficient increases significantly with increasing chlorine content. Other studies have shown that the major product of this reaction is production of the chloride anion so it is not surprising that the rate coefficient is strongly dependent on the number of chlorine atoms.<sup>5</sup> The reaction can be written as



where (chloroethane-Cl)\* is the chloride ion elimination product. The high solubility of the chloride anion aids in the energetics of the reaction. Formation of  $\text{Cl}^-$  is associated with the hydronium ion, which is the complementary oxidizing species associated with the hydrated electron, and is a major cause of radiolytically induced environmental corrosion.

Experiments using the two dichloroethanes were performed in ethanol in addition to water. Chloroethanes are more soluble in ethanol than in water and less likely to evaporate during the course of the experiment. Another potential problem in determining rate coefficients in water is that the chloroethane may cluster due to a hydrophobic effect, resulting in a lower effective concentration of the solute.<sup>15</sup> Such a phenomenon is not expected in ethanol. The similarity in rate coefficients between the aqueous and ethanol solutions gives confidence that the chloroethane concentrations are accurate and any clustering is minimal.

Hexachloroethane is very insoluble in water, so measurements of the solvated electron reactions were performed in various ethanol–water mixtures. For 1 mM hexachloroethane, a water volume fraction of up to 50% resulted in solutions with no apparent phase separation. Hexachloroethane is a solid, and its precipitation is visually obvious in mixtures containing high

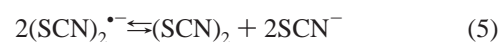
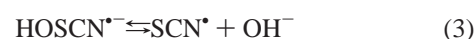
water content. However, dimerization or the formation of other small conglomerations would not be detected easily. Determination of the solvated electron rate coefficient with hexachloroethane gives values of  $1.15 \times 10^{10}$  to  $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in mixtures of 0 to 50% water by volume in ethanol, which essentially implies there is no variation in the rate coefficient with water/ethanol fraction. Increasing the solubilization times or additional stirring had no effect on the rate coefficient. In addition to the ethanol mixtures, a 40% *tert*-butyl alcohol mixture was also examined. A previous study with 40% *tert*-butyl alcohol reported a rate coefficient ( $3.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ), which is almost 1 order of magnitude greater than the value found in this work ( $4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), suggesting a typographical error.<sup>4</sup> Other experiments found rate coefficients for the solvated electron with hexachloroethane of  $1.6 \times 10^{10}$  and  $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in neat methanol and 2-propanol, respectively. The estimated rate coefficient of  $1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for the hydrated electron with hexachloroethane in water is 75% of that for pentachloroethane and lower than would be predicted from the observed trend with an increasing number of chlorine atoms, as shown in Figure 3. Similar diffusivities of the reactants and similar energetics of the reactants and products are expected for the solvated electron reaction with both pentachloroethane and hexachloroethane. The slower rate with hexachloroethane must be due to the high energy of formation for the electron adduct transition complex. A similar trend is observed in the rate coefficients of the methane analogues; i.e., the rate coefficient increases almost linearly from chloromethane to chloroform and then drops by a factor of 2 from chloroform to carbon tetrachloride. This result also suggests that the fully chlorinated alkane is stable toward the formation of an electron adduct.

The present results for the hydrated electron rate coefficients are in general agreement with the results published by Asmus and co-workers with the exception of the 1,1-dichloroethane.<sup>4</sup> However, some of the other measured rate coefficients are very different from those in the literature. Possible reasons for the discrepancies were noted above and include evaporation of the solute or hydrolysis. The former leads to a low rate coefficient and was found to be common when attempts to deaerate the sample were made. All previous studies used deaerated samples, and overestimations of the chloroethane concentrations are possible. Some of the chloroethanes, such as 1,1-dichloroethane, readily hydrolyze, and considerable care must be taken to examine fresh samples. Hydrolysis of chloroethanes produces the hydronium ion,  $\text{H}_{\text{aq}}^+$ , which readily reacts with the hydrated electron with a rate coefficient equal to  $2.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>3</sup> Ion chromatographic analyses for  $\text{Cl}^-$  were made on the samples before and after irradiation, assuming  $[\text{Cl}^-] = [\text{H}_{\text{aq}}^+]$ , to ensure the concentration of the hydronium ion was sufficiently low to avoid competition with the chloroethane for the hydrated electron.

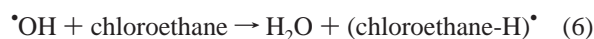
**Hydroxyl Radical Reactions.** Hydroxyl radicals are difficult to observe directly in the radiolysis of water. Reactions of OH radicals are usually examined in competition with a solute that has well-established chemistry. The solute used commonly for this purpose is the thiocyanate anion,  $\text{SCN}^-$ . A recent study reexamined the kinetics of this system and arrived at a consistent set of rate coefficients for the reactions involved.<sup>12</sup> The study also found that caution must be exercised in obtaining rate coefficients from simple exponential fits to the kinetic traces at low concentrations of  $\text{SCN}^-$  because of several equilibria reactions leading to formation of the observed dimer anion. Simulations in combination with experiment have shown that

a simple exponential fit to the data obtained from nitrous oxide saturated 0.1 mM  $\text{SCN}^-$  solutions is in error by about 10%.<sup>12</sup> High concentrations of  $\text{SCN}^-$  could not be used in the present experiments because of the low solubility of the chloroethanes, so the decay rates were analyzed by comparing the kinetic traces with the predictions of a model that was simulated using two different techniques. One simulation used the Chemical Kinetics Simulator 1.0 from IBM Almaden Research Center, which employs a stochastic Monte Carlo technique to follow the reactions of an ensemble of species.<sup>16</sup> The second calculation involved the FACSIMILE code by MCPA Software Ltd., which is a numerical method of solving simultaneous differential equations. Both techniques utilized homogeneous kinetics, employed the same reaction scheme, and optimized the rate coefficient to the best fit of the experimental trace. The resulting rate coefficients were within 1% of each other using both simulation techniques.

The chemistry of the thiocyanate with OH radicals proceeds according to the following reaction scheme,



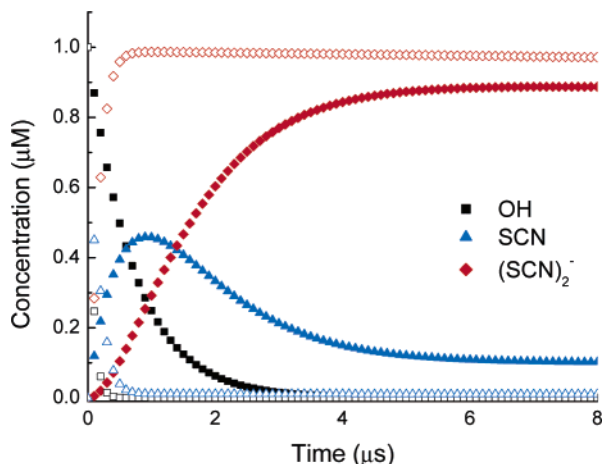
where  $k_2 = 1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ;<sup>12</sup>  $k_3 = 2 \times 10^8 \text{ s}^{-1}$ , with  $K_3 = 3.2 \times 10^{-2} \text{ M}$ ;<sup>17,18</sup>  $k_4 = 9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , with  $K_4 = 2 \times 10^5 \text{ M}^{-1}$ ;<sup>18–20</sup> and  $k_5 = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>12</sup> These reactions of the thiocyanate are coupled with the competing reaction of the OH radical with the chloroethane,



where (chloroethane-H)<sup>•</sup> is the H atom elimination product.<sup>4–6</sup> Examination of the  $(\text{SCN})_2^{\bullet-}$  formation kinetics at 472 nm with various concentration of the chloroethane allows accurate determination of the associated rate coefficient for reaction 6.

Hydroxyl radical rate coefficient measurements using competition kinetics with  $\text{SCN}^-$  can be performed either in laser photolysis or pulse radiolysis experiments. In the former, the OH radical is often produced by  $\text{H}_2\text{O}_2$  photolysis, while in the latter the OH radical is produced by radiolytic decomposition of the water. To double the OH radical concentration in radiolysis, which results in improved signal-to-noise ratio and smaller experimental error, the hydrated electrons are often converted to OH radicals by reaction with  $\text{N}_2\text{O}$ . However, the latter reaction is on a comparable time scale to many of the reactions examined here, and it introduces an increased level of complexity. Purging with  $\text{N}_2\text{O}$  can also result in evaporation of the chloroethane. The competition experiments for examining OH radical reactions were performed in aerated solutions to avoid decreasing the chloroethane concentration by deaeration. Furthermore, the oxygen is an effective sink for some of the hydrated electrons.

Typically, the kinetics of reactions 2–5 are simplified assuming consecutive forward reactions with no contribution by the back-reactions of the equilibria.<sup>11</sup> This oversimplification leads to the conclusion that the maximum  $(\text{SCN})_2^{\bullet-}$  concentration is equivalent to that of the initial OH radical concentration. Conditions are usually adjusted so that the  $(\text{SCN})_2^{\bullet-}$  decay due to reaction 5 is negligible. Reactions 2–5 are thereby reduced to a simple scavenging reaction of OH radical by the  $\text{SCN}^-$



**Figure 4.** Kinetic simulation of the decay of initial 1  $\mu\text{M}$  OH radical and the formation of  $\text{SCN}\bullet$  and  $(\text{SCN})_2^{\bullet-}$  for 0.1 mM (closed symbols) and 1.0 mM (open symbols)  $\text{SCN}^-$  solutions.

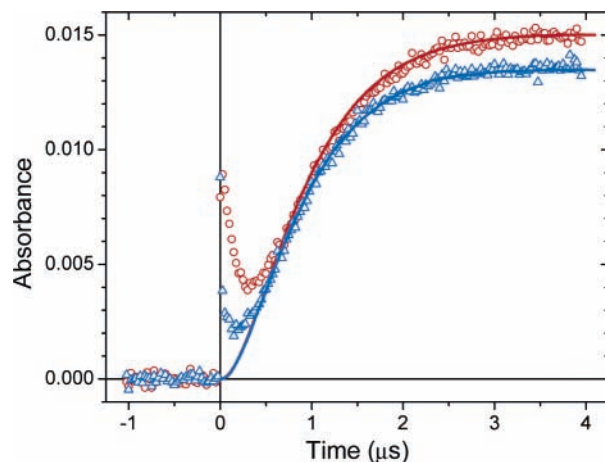
with the resulting kinetics given by



$$\frac{A_0}{A} = 1 + \frac{k_6 [\text{chloroethane}]}{k_7 [\text{SCN}^-]} \quad (8)$$

where  $A_0$  is the absorbance of  $(\text{SCN})_2^{\bullet-}$  in the absence of the chloroethane and  $A$  is absorbance of  $(\text{SCN})_2^{\bullet-}$  in the presence of the chloroethane.<sup>11</sup> A previous experimental-with-model study showed that the equilibria of reactions 3 and 4 cannot be ignored.<sup>12</sup> The results of kinetic simulations using reactions 2–5 with an initial OH concentration of 1  $\mu\text{M}$ , typical of a radiolysis experiment, and with different  $\text{SCN}^-$  concentrations are shown in Figure 4. A concentration of 1 mM  $\text{SCN}^-$  leads to the formation of  $(\text{SCN})_2^{\bullet-}$  that is within a few percent of the initial OH radical yield, but at a concentration of 0.1 mM  $\text{SCN}^-$  the formation of  $(\text{SCN})_2^{\bullet-}$  is 89% of the initial OH radical yield. The  $(\text{SCN})_2^{\bullet-}$  concentration is only about 43% of the initial OH radical yield at 0.01 mM  $\text{SCN}^-$ ; results not shown. Calculations show that  $\text{SCN}^-$  concentrations above 1 mM are required to drive the equilibria in reactions 3 and 4 sufficiently to the right that eqs 6 and 7 are reasonably representative of the system. Unfortunately, the use of competition kinetics for solutes with low rate coefficients requires the use of low  $\text{SCN}^-$  concentrations because of the limited solubility of the chloroethanes, and a true model simulation fitting of the experimental decay traces must be performed. A dependence of  $(\text{SCN})_2^{\bullet-}$  on the initial OH radical yield is observed if it is within 10% of the  $\text{SCN}^-$  concentration so a dose rate effect may be observed in certain situations.

Figure 5 shows the absorption of  $(\text{SCN})_2^{\bullet-}$  at 472 nm with and without added 1,1,2,2-tetrachloroethane. The initial decay is due to the tail of the hydrated electron peaked at 720 nm and extending beyond 472 nm. This decay is rapid due to the presence of oxygen and essentially over within a microsecond. A lower absorption is observed with added chloroethane because it is competing with the oxygen for the hydrated electron. The buildup of  $(\text{SCN})_2^{\bullet-}$  is observed on the microsecond time scale. Simulations of the kinetic model consisting of reactions 2–6 give optimized fits to the traces with the rate coefficients given in Table 1. In some cases, very low concentrations of  $\text{SCN}^-$  were required because of the very low OH radical reaction rates. The traces in these experiments showed additional decay of the  $(\text{SCN})_2^{\bullet-}$  that could not be accounted for in the reaction scheme



**Figure 5.** Absorbance of  $(\text{SCN})_2^{\bullet-}$  at 472 nm in aerated 0.2 mM  $\text{SCN}^-$  solutions with (O) 0.0 or ( $\Delta$ ) 14 mM of 1,1,2,2-tetrachloroethane. The solid lines are obtained from a simulated model fit to the data.

(2)–(5) given above. These conditions required the addition of two more reactions,



where  $k_9 = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{10} = 2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  as obtained from optimized fitting of the model to the decay traces. With the inclusion of these reactions, it is possible to correctly reproduce the increase in the decay of  $(\text{SCN})_2^{\bullet-}$  experimentally observed on the microsecond time scale.

The rate coefficients given in Table 1 for the reactions of OH radicals show wide variations with the number of chlorine atoms. This reaction is an H atom abstraction reaction, and the type of C–H bond has a significant effect on the reaction rate. For instance, the rate coefficient for 1,1,2-trichloroethane is  $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , while that for 1,1,1-trichloroethane is less than  $5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . 1,1,1-Trichloroethane contains three primary C–H bonds that are relatively less reactive than the two secondary and one tertiary C–H bonds in 1,1,2-trichloroethane. A similar effect is observed for the tetrachloroethanes. There is no correlation between the OH radical reaction rates and those of the hydrated electron, which is to be expected since the mechanisms are very different. The former is an H atom extraction reaction possibly preceded by the formation of a bridged transition state.<sup>21</sup> The other reaction is an electron addition in conjunction with bond cleavage, which can be enhanced in the aqueous phase by the high solubility of the products. The reaction rate of the OH radicals with monochloroethane is about three times faster than that of the hydrated electron. With increasing number of chlorine atoms, the rate coefficients of the hydrated electron increase, while those of the OH radicals show no trend. The hydrated electron rate easily overtakes that of the OH radical for the bigger tetra- and pentachloroethanes, where more target chlorine atoms are available to capture and accept the electron. Except for those cases where no H atoms are available, the rate coefficients for OH radicals are very nearly the same for all the chloroethanes.

For the most part, the OH radical rate coefficients found here are in agreement with those in the literature. The present results tend to be lower where discrepancies do occur. Very few details are given of the analysis techniques used to obtain the rate coefficients presented in the literature, but it does not appear that model simulations were used. As discussed above, the use

of very low  $\text{SCN}^-$  concentrations requires the modeling of the complete system because of the equilibria involved.

**H Atom Reactions.** Since H atoms make up a small portion of the radiolytic products in the radiolysis of water, measurements of their rate of reaction with the chloroethanes was attempted. In general, the rates were low, less than  $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  as determined using competition studies with  $\text{SCN}^-$ . These rates are too low to measure accurately using  $\text{SCN}^-$  competition kinetics. Literature values are  $1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for monochloroethane and  $2.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for 1,2-dichloroethane.<sup>8,5</sup> Other methods such as time-resolved EPR offer far better approaches for performing these measurements.

## Conclusion

Pulse radiolysis techniques have been used to determine the rate coefficients of the hydrated electron and OH radical with various chloroethanes in water. Direct observation of the hydrated electron decay shows that the rate coefficient increases by about an order of magnitude with increasing number of chlorine atoms on the chloroethane. Competition kinetics using  $\text{SCN}^-$  are shown to be suitable for OH radical measurements if suitable precautions are used at low  $\text{SCN}^-$  concentrations. The OH radical reaction with the chloroethanes is nearly independent of the number of chlorine atoms except when no H atoms are available on a carbon atom. OH radicals react by H atom abstraction and the presence of an H atom has a significant effect on the rate coefficient.

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