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Pulse Radiolysis of Aqueous Thiocyanate Solution

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The pulse radiolysis of N_2O saturated aqueous solutions of KSCN was studied under neutral pH conditions. The observed optical absorption spectrum of the $SCN^\bullet$ radical in solution is more complex than previously reported, but it is in good agreement with that measured in the gas phase. Kinetic traces at 330 and 472 nm corresponding to $SCN^\bullet$ and $(SCN)_2^{\bullet-}$, respectively, were fit using a Monte Carlo simulation kinetic model. The rate coefficient for the oxidation of SCN^- ions by OH radicals, an important reaction used in competition kinetics measurements, was found to be $(1.4 \pm 0.1) \times 10^{10}\ M^{-1}\ s^{-1}$, about 30% higher than the normally accepted value. A detailed discussion of the reaction mechanism is presented.

Introduction

As a result of their importance in organic chemistry, molecular biology, and medicine, reactions involving hydroxyl radicals have been studied extensively.[1] Knowledge of accurate values for the rate coefficients of these reactions is often critical in determining overall mechanisms in complex systems. Pulse-radiolysis experimental techniques are commonly used for measuring the rate coefficients of OH radical reactions. The energy of ionizing radiation is mainly deposited in the water molecules leading to OH radical formation on the picosecond time scale.[2,3] Because of the low extinction coefficient ($\epsilon = 575\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 230$ nm) and spectral overlap with other reactants, direct spectroscopic measurements of the OH radical are not practical in most cases.[4] An alternative method for determining OH radical rate coefficients is to use competition kinetics, the most frequently used reagent being the thiocyanate anion. However, interpretation of the results using this reaction may involve some ambiguities regarding the value of the rate coefficient of the $OH + SCN^-$ reaction as reviewed below.

The mechanism for the radiolysis of aqueous solutions of SCN^- was first reported by Adams et al.[5] Pulse-radiolysis measurements show the formation of a transient species ($\lambda = 480$ nm) in SCN^- reaction with OH radical, which was initially assigned to the $SCN^\bullet$ radical.

$$^\bullet OH + SCN^- \rightarrow SCN^\bullet + OH^- \qquad (1)$$

In a subsequent study,[6] the authors pointed out that the experimental data would also be consistent with the transient species being $(SCN)_2^{\bullet-}$, produced in the secondary equilibrium reaction of $SCN^\bullet$ with SCN^-.

$$SCN^\bullet + SCN^- \rightarrow (SCN)_2^{\bullet-} \qquad (2)$$

Later pulse-radiolysis studies by Baxendale and co-workers on transient formation at low SCN^- concentrations produced results that conclusively prove the absorption at 480 nm is due to $(SCN)_2^{\bullet-}$.[7,8] The rate coefficient corresponding to reaction 1 was reported to be $2.8 \times 10^{10}\ M^{-1}\ s^{-1}$, and the equilibrium constant was $K_2 = 2 \times 10^5\ M^{-1}$. The effect of ionic strength proved that $(SCN)_2^{\bullet-}$ is involved in a second-order reaction to give $(SCN)_2$ and SCN^-.

Scholes and co-workers further investigated the oxidation of SCN^- ions by OH radicals and discovered several equilibria involved in the mechanism.[9] The mechanism for reaction 1 first involves the formation of an adduct,

$$^\bullet OH + SCN^- \rightarrow HOSCN^{\bullet-} \qquad (3)$$

the dissociation of which is pH dependent.

$$HOSCN^{\bullet-} \leftrightarrows SCN^\bullet + OH^- \qquad (4)$$

The equilibrium constant for reaction 2 was found to be $K_2 = 2 \times 10^5\ M^{-1}$, while that for reaction 4 was found to be $K_4 = 3.2 \times 10^{-2}\ M^{-1}$. As pointed out by Baxendale et al., this work also showed that the thiocyanate dimer radical anion recombines by

$$2(SCN)_2^{\bullet-} \rightarrow (SCN)_2 + 2SCN^- \qquad (5)$$

so that the thiocyanate dimer is the final stable radiolysis product. The concentration of $(SCN)_2^{\bullet-}$ is usually constant on the microsecond time scale making this system suitable for absolute dosimetry.

A variety of studies tried to measure the rate coefficient corresponding to reaction 3 using the competition kinetics method. In this method, the transient species in reaction with a solute for which the rate coefficient is not known is compared to its reaction with another solute with an accurately known rate coefficient. Zehavi and Rabani used the reference reactions of the OH radical with ethanol and with methanol to give values of 1.0×10^{10} and $1.1 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively, for reaction 3.[10] The solute concentration dependence of the measured rate coefficient was noted, but no explanation was offered. Dorfman et al. used the competition kinetics of OH radicals with ferrocyanide and thymine and obtained the values of 1.1×10^{10} and $9 \times 10^9\ M^{-1}\ s^{-1}$, respectively, for reaction 3.[11] Elliot and Simsons used $OH + HCOO^-$ as a reference reaction to obtain $1.08 \times 10^{10}\ M^{-1}\ s^{-1}$ for the rate coefficient of reaction 3 at 18 °C.[12]

Wilkinson and co-workers also studied the oxidation of SCN^- by OH radicals using nanosecond pulse radiolysis.[13] They irradiated 0.5 and 1.2 mM KSCN solutions with 10 or 25 ns pulses and monitored the buildup of $(SCN)_2^{\bullet-}$ at 475 nm. From

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a fit of the oscilloscope traces obtained to a (simplified) kinetic model, the rate coefficients for reactions 2 and 3 were estimated to be $(1.08 \pm 0.10) \times 10^{10}$ M^{-1} s^{-1}. A similar experiment was performed by Tanaka and co-workers who obtained the value of 1.0×10^{10} M^{-1} s^{-1} for reaction 3.[14]

Chin and Wine used laser photolysis to produce OH radicals in the photolysis of H_2O_2.[15] The buildup kinetics of $(SCN)_2^{\bullet -}$ was monitored at 475 nm, and the traces obtained were fitted to a kinetic model to give a rate coefficient for reaction 3 of 1.3×10^{10} M^{-1} s^{-1} at 22 °C. Motohashi and Saito measured the rate coefficient corresponding to reaction 3 using a steady-state γ radiolysis competition kinetics method.[16] The reference reaction was OH + $C_6H_5CO_2^-$, and they obtained a value of 1.2×10^{10} M^{-1} s^{-1} at room temperature and pH = 7.5.

In all of these pulse-radiolysis or laser-photolysis experiments, only the observed trace at about 475 nm corresponding to the $(SCN)_2^{\bullet -}$ formation was fitted to a kinetic model. The models differed slightly but could contain up to three variables. The Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (OH/O^-) in Aqueous Solution selects the value of $k_3 = 1.1 \times 10^{10}$ M^{-1} s^{-1} with no stated reason but presumably from a consensus of most of the experimental values.[17] In general, fitting one kinetic trace to an equation with three variables can produce several combinations of parameters each giving an apparent excellent fit. Another independent set of kinetics would result in more accurate rate coefficients for an important chemical reaction. Modern digital data acquisition and signal averaging that takes into account dose variation and other parameters can give much higher accuracy than was possible a few decades ago. Transients with low extinction coefficients at relatively low concentrations (such as the trace at 330 nm corresponding to the thiocyanate radical) can be readily monitored.

In this work, kinetic traces at 330 and 472 nm corresponding to the thiocyanate radical and thiocyanate dimer radical anion, respectively, were obtained. The rate coefficient corresponding to the OH radical with SCN^-, reaction 3, was obtained by fitting the kinetic traces corresponding to $SCN^\bullet$ and $(SCN)_2^{\bullet -}$ to a complete kinetic model using a Monte Carlo simulation method.

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). Details of the linac, the spectrophotometric detection setup, and the computer-controlled data acquisition and detection systems are described elsewhere.[18] All measurements were performed at 20 °C in a high-purity silica cell of 1 cm optical path length. The concentration of radicals generated was approximately 4.0 μM per pulse with a dose of about 7 Gy (700 rad) per pulse, as determined by the thiocyanate dosimeter. All solutions were deaerated by bubbling N_2O for at least 30 min immediately prior to irradiation.

KSCN (Aldrich) was of the highest purity commercially available and used as received. Water was purified using an H_2Only system, which is a commercial arrangement consisting of a UV lamp, microfilters, and ion-exchange resins. A kinetic trace of the decay of the hydrated electron in neat water showed no sign of impurities that could interfere in these experiments.

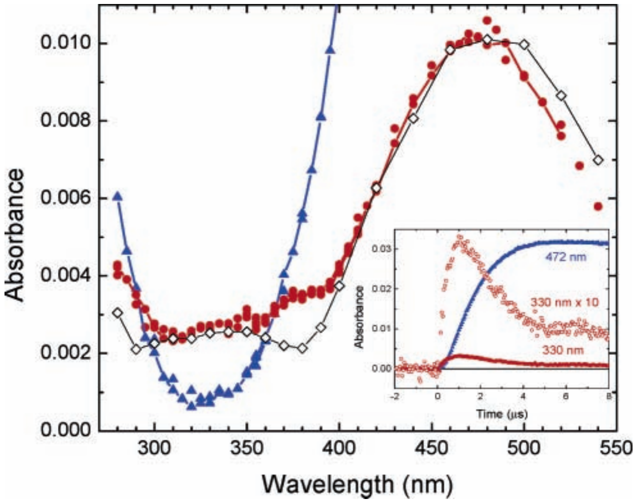

Figure 1. Transient absorption spectra in pulsed aqueous 0.1 mM KSCN solutions at natural pH: (●) spectrum after 1 μs; (▲) spectrum after 5 μs (480 nm peak maximum), this work; (◇) normalized data of Figure 1 in ref 9. Inset shows traces at selected wavelengths; 330 nm rescaled trace is also shown to illustrate the kinetics.

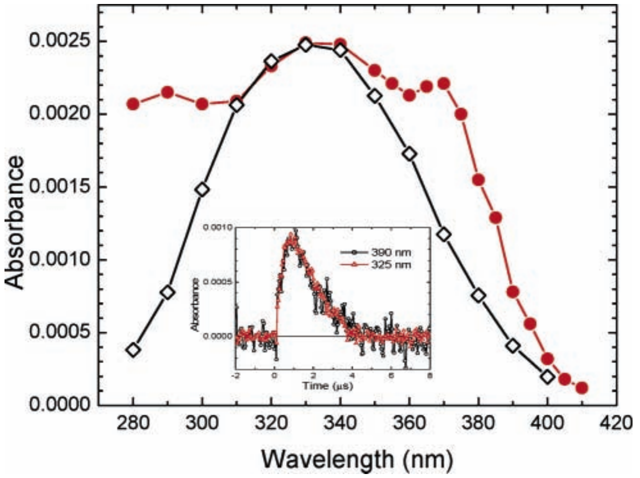

Figure 2. Spectra of $SCN^\bullet$: (●) this work; (◇) ref 9. Inset compares kinetics at 325 and 390 nm corrected for background absorption of $(SCN)_2^{\bullet -}$.

Results and Discussion

The best methods to determine the rate coefficient of reaction 3 are to measure the change in rate of decay of the OH radical or the rate of formation of $HOSCN^-$. The OH radical has a low extinction coefficient ($\epsilon = 575$ M^{-1} cm^{-1} at $\lambda_{max} = 230$ nm) and spectral overlap with other transient water products, making its direct observation very difficult. Absorption of $HOSCN^{\bullet -}$ is reported to occur at about 390 nm, as identified in very basic solutions where the back reaction is significant.[9] The lifetime of $HOSCN^{\bullet -}$ is estimated to be 5 ns, which is much too short to be observed on the time scales examined here.[13] The next transient species to be formed in the reaction scheme is the thiocyanate radical, $SCN^\bullet$. Figure 1 shows the observed transient absorption spectra in pulsed aqueous 0.1 mM KSCN solutions at natural pH. The solutions were saturated with N_2O to convert the hydrated electron to OH radicals. The spectrum obtained 1 μs after the pulse is compared in Figure 1 with one published in ref 9. Significant difference is observed in the spectral region from 280 to 400 nm. The spectra from 5 to 150 μs have essentially the same shape indicating that the species observed at about 330 nm has completely reacted in a few microseconds. Normalization of the two spectra in Figure 1 at 480 nm and subtraction give the difference spectra as shown in Figure 2. The spectrum from the present work exhibits a complex structure, while the spectrum from ref 9 comprises a single (Gaussian) band centered at 330 nm. Gas-phase measurements of the electronic absorption spectrum of the $SCN^{\bullet}$ free radical show strong transitions around 380 nm, which is in agreement with the present results.[19] The inset in Figure 2 compares the kinetic traces at 325 and 390 nm corrected for the $(SCN)_2^{\bullet -}$ background absorption. The identical kinetics confirms that the spectrum corresponds to only one species, that is, $SCN^{\bullet}$. The discrepancy in the spectra is due to the more sophisticated detection system in the present work that allows precise measurements with less noise.

The inset in Figure 1 compares the experimental traces at 330 and 472 nm. One can readily see the formation of the transient at 330 nm followed by its decay and the concurrent formation of the species at 472 nm. An apparent plateau of the 330-nm trace at long times is due to the background from the tail of the 472-nm peak. Subtraction of the long-time limit shows that the 330-nm trace decays to zero within 10 μs. The complementary kinetics strongly suggests that the species absorbing at 330 nm is a precursor to the $(SCN)_2^{\bullet -}$ absorbing at 472 nm. From simple statistical arguments, backed by Monte Carlo calculations, one expects that the additional kinetics for the precursor to $(SCN)_2^{\bullet -}$ will give much more reliable data for the rate coefficient of reaction 3.

The experimentally obtained traces at 330 and 472 nm for $SCN^{\bullet}$ and $(SCN)_2^{\bullet -}$, respectively, were fitted using Chemical Kinetics Simulator 1.0 from IBM Almaden Research Center. The main reaction scheme consisted of reactions 2−4 with the following coefficients: $k_2 = 9 \times 10^9$ M^{-1} s^{-1}, with $K_2 = 2 \times 10^5$ M^{-1};[8,9,20] $k_4 = 2 \times 10^8$ s^{-1}, with $K_4 = 3.2 \times 10^{-2}$ M^{-1}.[9,13] The value of k_2 from ref 8 was used instead of others in the literature because that experiment involved the photolysis of $(SCN)_2^{\bullet -}$, which was more straightforward than most of the other experiments. That value also gave a perfect fit to the present results. Additional reactions must be considered, since the system is saturated (26 mM) in N_2O,

$$e_{aq}^{-} + N_2O \rightarrow N_2 + O^{\bullet -} \tag{6}$$

$$O^{\bullet -} + H_2O \rightarrow {}^{\bullet}OH + OH^{-} \tag{7}$$

with $k_6 = 9.1 \times 10^9$ M^{-1} s^{-1} and $k_7 = 1.7 \times 10^6$ M^{-1} s^{-1}.[17] Oxygen atom anion can possibly react with SCN^- at high concentrations by the following:

$$O^{-} + SCN^{-} \rightarrow SCNO^{2-} \tag{8}$$

with $k_8 = 1.4 \times 10^9$ M^{-1} s^{-1}.[10] At the highest SCN^- concentrations used here, 2 mM, only a few percent of the oxygen atom anions follow reaction 8, so it has been ignored in the present calculations. Absorbances were converted into concentrations by dividing with the corresponding extinction coefficients. The $SCN^{\bullet}$ extinction coefficient at 330 nm (1200 M^{-1} cm^{-1}) was taken from ref 20, and the $(SCN)_2^{\bullet -}$ extinction coefficient at 472 nm (7580 M^{-1} cm^{-1}) was taken from ref 21. The yield of hydrated electrons was taken as 3.4 electrons per 100 eV in agreement with the experiment.[22] The OH radical yield was taken to be 2.73 radicals per 100 eV to give agreement with the total value of 6.13 obtained by Schuler et al.[21] The results of the model calculations are reported without additional scaling.

At long times (>10 μs), $(SCN)_2^{\bullet -}$ decays by the second-order process given by reaction 5. This decay is so slow in the present system that it could be treated separately from its formation processes. A rate coefficient of 1.2×10^9 M^{-1} s^{-1} was obtained from a best fit to the decay traces. The only variable left in the formation of $(SCN)_2^{\bullet -}$ is the rate coefficient for reaction 3, which was found by the best fit using the IBM Monte Carlo code.

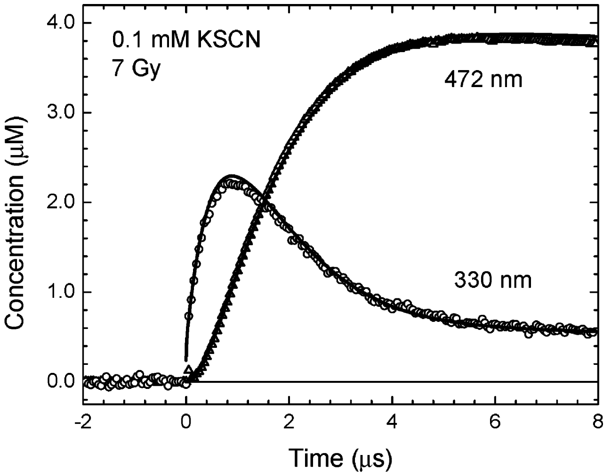

Figure 3. Transient absorption traces in pulsed aqueous KSCN solutions (0.1 mM) at natural pH divided by the corresponding extinction coefficients: (○) 330 nm; (△) 472 nm. Solid lines represent the computer generated kinetic curves using $k_3 = 1.4 \times 10^{10}$ M^{-1} s^{-1}.

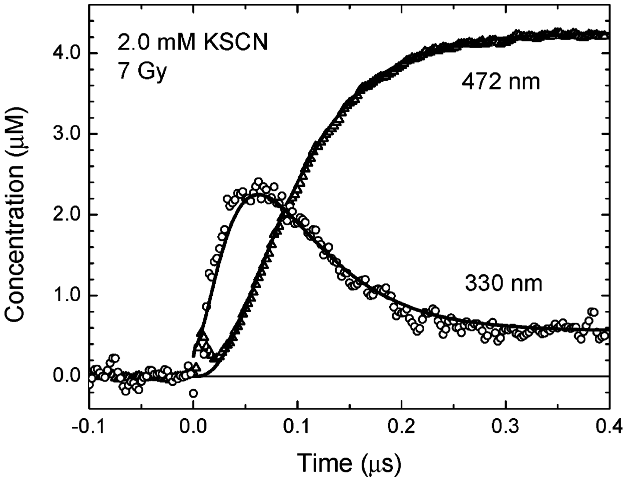

Figure 4. Transient absorption traces in pulsed aqueous KSCN solutions (2.0 mM) at natural pH divided by the corresponding extinction coefficients: (○) 330 nm; (△) 472 nm. Solid lines represent the computer generated kinetic curves using $k_3 = 1.4 \times 10^{10}$ M^{-1} s^{-1}.

The results of the Monte Carlo fitting to the kinetic traces are shown in Figures 3 and 4 for initial KSCN concentrations of 0.1 and 2 mM, respectively. It can be seen that the results of the simulation fit the experimental traces very well using a value of $k_3 = 1.4 \times 10^{10}$ M^{-1} s^{-1}. Variation of the simulation parameters indicate that matching the trace at 330 nm has a much more critical effect on the value of the rate coefficient of reaction 3 than the trace at 472 nm. Including the measurement at 330 nm for $SCN^{\bullet}$ into the mechanism greatly enhances the precision for determining the rate coefficient of reaction 3. Such a result is intuitive, since one expects examination of the products more directly related to the adduct formed from OH radical addition to SCN^- will give a better representation of the kinetics of this reaction. The value for OH addition to SCN^- determined in this work is some 30% higher than the selected value most often used.[17]

Conclusion

A consistent set of reaction parameters in the pulse radiolysis of SCN^- was obtained by fitting the experimentally measured kinetic traces at 330 nm, $SCN^\bullet$, and at 472 nm, $(SCN)_2^{\bullet-}$. The rate coefficient for the oxidation of SCN^- by OH radicals, an important reaction used in competition kinetics measurements, was found to be $(1.4 \pm 0.1) \times 10^{10}$ M^{-1} s^{-1}. This rate coefficient is 30% higher than the commonly accepted value, which may have important consequences in describing complex systems involving competing reactions of OH radicals. The optical absorption spectrum of $SCN^\bullet$ is more complex than previously reported but is in good agreement with a gas-phase measurement.

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