J. Phys. Chem. A **2005,** *109,* 11823−11827

Rate Constant and Activation Energy Measurement for the Reaction of Atomic Hydrogen with Thiocyanate and Azide in Aqueous Solution

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Received: September 26, 2005; In Final Form: October 25, 2005

Arrhenius parameters for the reaction of hydrogen atoms with azide and thiocyanate in aqueous solution have been determined using electron pulse radiolysis and electron paramagnetic resonance free induction decay attenuation measurements. Absolute values for SCN^-, N_3^-, and HN_3 were well-described over the temperature range of 9−81 °C by the equations $\log k_5 = (12.03 \pm 0.12) - [(21.05 \pm 0.66\ \text{kJ mol}^{-1})/2.303RT]$, $\log k_{10} = (12.75 \pm 0.21) - [(18.43 \pm 1.22\ \text{kJ mol}^{-1})/2.303RT]$, and $\log k_{15} = (11.59 \pm 0.12) - [(21.44 \pm 0.69\ \text{kJ mol}^{-1})/2.303RT]$, corresponding to room temperature (22 °C) rate constants of $(2.07 \pm 0.03) \times 10^8$, $(3.15 \pm 0.08) \times 10^9$, and $(6.31 \pm 0.05) \times 10^7\ M^{-1}\ s^{-1}$ and activation energies for these chemicals of 21.05 ± 0.66, 18.4 ± 1.2, and 21.44 ± 0.69 kJ mol^{-1}, respectively. The similarity of these three measured activation energies, taken together with the available information on reaction products, suggests a similar reaction mechanism, which is proposed to be an initial hydrogen atom adduct formation in these molecules, followed by single bond breakage.

Introduction

Over the past 16 years the temperature-dependent kinetics of the hydrogen atom reaction with a variety of organic and inorganic chemicals in water has been investigated using the pulsed electron paramagnetic resonance (EPR)-based free induction decay (FID) attenuation method.[1−17] For most of the organic compounds studied, especially the low molecular weight alcohols,[6,11,14] acids,[15,17] and carbonyls,[8,13,16] these investigations reported Arrhenius parameters ($E_a \sim 20{-}30$ kJ mol^{-1}, $A \sim 10^{11-13}\ M^{-1}\ s^{-1}$) consistent with simple hydrogen atom abstraction from C−H bonds. For the analogous reaction of hydrogen atoms with deuterated organic compounds,[15−17] the corresponding activation energies were found to be approximately 4−6 kJ mol^{-1} larger. Lower activation energies ($\sim 11 \pm 1$ kJ mol^{-1}) were measured for the $H^\bullet$ atom reaction with iodoalkanes,[6] where halogen abstraction was believed to occur, and higher values ($\sim 30 \pm 3$ kJ mol^{-1}) were obtained for hydrogen atom abstraction from methyl groups in methanol,[6] formic acid,[15] and acetone,[8] as well as methanediol.[16]

However, the measured values for hydrogen atom reaction with some inorganic species were less consistent. In the reaction of the hydrogen atom with iodide and bromide ions in aqueous solution,[4,18] the temperature dependence of the rate constant was essentially found to be zero; the measured activation energies were $E_a = 1.8 \pm 4.6$ and 6.3 ± 6.2 kJ mol^{-1}, respectively. For hydrogen atom reaction with IO_3^- and IO_4^-,[7] the activation energies were found to be $E_a = 27.4 \pm 1.7$ and 22.4 ± 2.7 kJ mol^{-1}, but for the acid forms of these two species (HIO_3 and H_5IO_6), they were much higher at 36.5 ± 2.0 and 53.0 ± 8.0 kJ mol^{-1}, respectively.

Of particular interest in these hydrogen atom reactions with inorganic chemicals were the Arrhenius parameters obtained from the reaction with the nitrogen-containing chemicals hydrazine[10] (N_2H_4) and nitrate/nitrite ($NO_3^-/NO_2^-/HNO_2$).[12] These values are listed in Table 1. For the nonprotonated form (N_2H_4), the Arrhenius parameters of $E_a = 16.3 \pm 0.8$ kJ mol^{-1}/$A = 4.8 \times 10^{10}\ M^{-1}\ s^{-1}$ were consistent with the standard hydrogen atom abstraction to form H_2 and the $^\bullet N_2H_3$ radical species:[10]

$$H^\bullet + N_2H_4 \rightarrow {}^\bullet N_2H_3 + H_2 \tag{1}$$

However, in more acidic solutions, where $N_2H_5^+$ was present, the temperature-dependent reaction rate constant was found to have Arrhenius parameters that were far larger: $E_a = 61.4 \pm 1.2$ kJ mol^{-1}/$A = 9.0 \times 10^{16}\ M^{-1}\ s^{-1}$. This large difference was proposed to be due to a change in the reaction mechanism, from hydrogen atom abstraction to N−N bond cleavage:

$$^\bullet H + N_2H_5^+ \rightarrow {}^\bullet NH_2 + NH_3 + H^+ \tag{2}$$

This mechanism change was later supported by high-level ab initio calculations.[19]

Similar large Arrhenius parameters were observed for hydrogen atom reaction with nitrate,[12] as compared to nitrous acid or the nitrite anion. For the latter two species, Arrhenius parameters of $E_a = 21.54 \pm 0.69$ kJ mol^{-1}/$A = 2.3 \times 10^{12}$ $M^{-1}\ s^{-1}$ and $E_a = 15.59 \pm 0.36$ kJ mol^{-1}/$A = 8.7 \times 10^{11}\ M^{-1}$ s^{-1} were consistent with the proposed mechanism of oxygen atom abstraction:

$$^\bullet H + (H)NO_2 \rightarrow {}^\bullet OH + (H)NO \tag{3}$$

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10.1021/jp055477h CCC: $30.25

TABLE 1: Summary of Arrhenius Parameters for Hydrogen Atom Reaction Rate Constants with Nitrogen-Containing Chemicals in Aqueous Solution

chemical	E_a (kJ mol^{-1})	$\log_{10} A$ (M^{-1} s^{-1})	comment/ref
N_2H_4	16.28 ± 0.80	10.69 ± 0.13	hydrogen atom abstraction reaction[10]
$N_2H_5^+$	61.4 ± 1.2	16.95 ± 0.18	N−N bond breakage, H^+ release[10]
NO_2^-	15.59 ± 0.36	11.94 ± 0.06	O-atom abstraction to form $^\bullet$OH[12]
HNO_2	21.54 ± 0.69	12.36 ± 0.12	O-atom abstraction to form $^\bullet$OH[12]
NO_3^-	48.7 ± 1.0	15.28 ± 0.16	O-atom abstraction to form $^\bullet$OH[12]
SCN^-	$\mathbf{21.05 \pm 0.66}$	$\mathbf{12.03 \pm 0.12}$	**this study**; $^\bullet$H-atom adduct formation
N_3^-	$\mathbf{18.4 \pm 1.2}$	$\mathbf{12.75 \pm 0.21}$	**this study**; $^\bullet$H-atom adduct formation
HN_3	$\mathbf{21.44 \pm 0.69}$	$\mathbf{11.59 \pm 0.12}$	**this study**; $^\bullet$H-atom adduct formation

For nitrate, the Arrhenius parameters were again much larger: $E_a = 48.7 \pm 1.0$ kJ mol^{-1}/$A = 1.9 \times 10^{15}$ M^{-1} s^{-1}. However, low-level ab initio calculations could not differentiate the reaction mechanism for all three of these chemicals.

To further investigate the behavior of aqueous hydrogen atom reaction with nitrogen-containing compounds, we have investigated the temperature-dependent rate constant for hydrogen atom reaction with thiocyanate (SCN^-) and azide (HN_3/N_3^-) in this study. These simple compounds were specifically chosen as their hydrogen atom reactions have previously been shown not to result in quantitative formation of H_2,[20,21] thus eliminating the standard reaction mechanisms of simple adduct formation followed by radical recombination, or hydrogen atom abstraction, and also because these particular chemicals are commonly used in radiation chemistry to provide clean one-electron oxidations (azide) and as a dosimetry standard (SCN^-).

Experimental Section

Potassium thiocyanate and sodium azide were obtained from the Aldrich Chemical Co. at the highest purity available. Both were used as received. Scavenging experiments were performed by successive weighted additions of these solids to a known volume (typically 160−170 mL) of ASTM type 1 water in a recirculating system that had been rigorously deaerated using argon or nitrous oxide (N_2O). The accuracy of these concentrations is estimated at better than 1%. For SCN^- and HN_3 experiments, the solution pH was adjusted to 2.00 using $HClO_4$. For N_3^-, buffered 0.010 M borate solutions at pH 9.1 were used. All solutions contained ~10^{-2} M methanol to help scavenge hydroxyl radicals produced in the radiolysis.

Hydrogen atoms were generated in aqueous solution within an EPR cavity by pulse radiolysis using 3 MeV electrons from a Van de Graaff accelerator at Argonne National Laboratory, near Chicago. The established pulsed EPR-based FID attenuation method was used,[1−4] because it directly monitors the aqueous $^\bullet$H atom and gives simple pseudo-first-order kinetics. This method involves a microwave probe pulse being applied to the sample immediately after irradiation, with the resulting FID of the $^\bullet$H atom low-field EPR transition being recorded on a digital oscilloscope. Typically, 500−2000 pulses were averaged to record each FID trace, at a repetition rate of 120 Hz.

Results and Discussion

Hydrogen Atom Reaction with Thiocyanate. The pK_a of thiocyanate is -1.1 ± 0.3;[22] and therefore, at pH 2.0, we only had deprotonated SCN^- species. Typical scavenging plots are shown in Figure 1a for the reaction of the aqueous hydrogen atom with thiocyanate at this pH and 22.0 °C. Although excellent linearity for these scavenging plots is observed, a slight dose dependence is evident from the fitted slopes of $(2.37 \pm 0.03) \times 10^8$, $(2.23 \pm 0.04) \times 10^8$, and $(2.11 \pm 0.06) \times 10^8$ M^{-1} s^{-1} for the 100, 55, and 25 ns pulses used, respectively. The general expression of the effective damping rate of the FID in these experiments is given by:[1−4]

$$k_{\mathrm{eff}} = k^{\mathrm{o}} + k_5[S] + \sum k_{\mathrm{ex}}{}^{i}[R_i] \tag{4}$$

where k^{o} is the first-order natural spin relaxation rate constant in the absence of added thiocyanate, $k_5[SCN^-]$ is the $^\bullet$H atom scavenging rate for the reaction

$$^\bullet H + SCN^- \rightarrow \text{products} \tag{5}$$

and $\sum k_{\mathrm{ex}}{}^{i}[R_i]$ represents the spin-dephasing contribution of the second-order spin exchange and recombination reactions between $^\bullet$H atoms and other free radicals. The observed dose dependence occurs when the latter term is not approximately constant over the 5 μs experimental time scale.

To correct our experimental rate constants for this dose dependence, limiting values were calculated by extrapolation to zero dose,[7−9] as shown in Figure 1b. The dose values used were simply the average beam currents measured on a shutter positioned before the irradiation cell for the three pulse widths. These currents were checked frequently to compensate for any

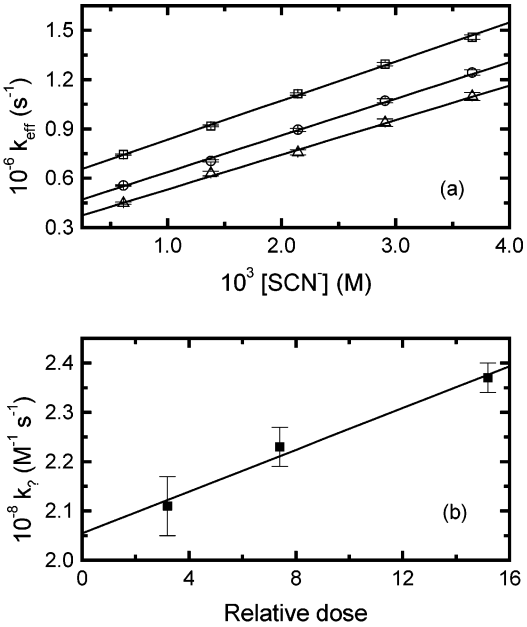

Figure 1. (a) Dose dependence of the aqueous hydrogen atom scavenging rate constant for SCN^- reaction at pH 2.0 and 22.0 °C. Data correspond to electron pulse widths of 100 (□), 55 (○), and 25 (△) ns. Error bars are one standard deviation, as derived from the damped cosine fits to individual FIDs. Solid lines are weighted linear fits, corresponding to specific reaction rate constants of $(2.37 \pm 0.03) \times 10^8$, $(2.23 \pm 0.04) \times 10^8$, and $(2.11 \pm 0.06) \times 10^8$ M^{-1} s^{-1}, respectively. (b) Extrapolation of dose-dependent rate constants. Intercept value corresponds to zero-dose, limiting value of $(2.07 \pm 0.03) \times 10^8$ M^{-1} s^{-1}.

TABLE 2: Summary of Temperature-Dependent Rate Constant Data for Hydrogen Atom Reaction with SCN^-, N_3^-, and HN_3 in Aqueous Solution

species	temp (°C)	scavenging rate constant (M^{-1} s^{-1})
SCN^-	9.1	$(1.35 \pm 0.02) \times 10^8$
	22.0	$(2.07 \pm 0.03) \times 10^8$
	43.4	$(3.80 \pm 0.14) \times 10^8$
	61.2	$(5.30 \pm 0.14) \times 10^8$
	78.3	$(8.38 \pm 0.55) \times 10^8$
N_3^-	8.8	$(1.96 \pm 0.12) \times 10^9$
	22.2	$(3.15 \pm 0.08) \times 10^9$
	42.5	$(5.36 \pm 0.22) \times 10^9$
	59.8	$(6.26 \pm 0.35) \times 10^9$
	82.7	$(1.04 \pm 0.08) \times 10^{10}$
HN_3	9.2	$(4.29 \pm 0.05) \times 10^7$
	22.6	$(6.31 \pm 0.05) \times 10^7$
	42.4	$(1.06 \pm 0.04) \times 10^8$
	59.9	$(1.72 \pm 0.21) \times 10^8$
	81.0	$(2.87 \pm 0.12) \times 10^8$

small drift in the beam. A very good linear extrapolation was obtained, with the limiting value for the addition reaction calculated as $(2.07 \pm 0.03) \times 10^8$ M^{-1} s^{-1} at this temperature (22.0 °C). This procedure was repeated over the temperature range of 9.1−78.3 °C, with all of the extrapolated rate constants summarized in Table 2 and shown in the Arrhenius plot in Figure 2. From a weighted linear fit of these data, the temperature-dependent rate constant is well-described by:

$$\log_{10} k_5 = (12.03 \pm 0.12) - [(21.05 \pm 0.66 \text{ kJ mol}^{-1})/2.303RT)] \quad (6)$$

A survey of the literature found two previous measurements for this reaction, both at room temperature (assumed to be 22 °C). Elliot et al.[20] measured a rate constant by directly monitoring the rate of formation of a transient (assumed to be $H(SCN)^{\bullet -}$ with $\lambda_{max} \sim 420$ nm and $\epsilon_{max} \sim 420$ M^{-1} cm^{-1}) and obtained a value of $k = (2.3 \pm 0.1) \times 10^8$ M^{-1} s^{-1}. There has also been one steady-state competition kinetics measurement of this hydrogen atom reaction rate constant,[21] where a comparable rate constant of 2.7×10^8 M^{-1} s^{-1} was determined using $(CH_3)_2CHOH$ as a standard. Both of these values are in very good agreement with our direct measurement at this temperature of $k_5 = (2.07 \pm 0.03) \times 10^8$ M^{-1} s^{-1} (also see Figure 2).

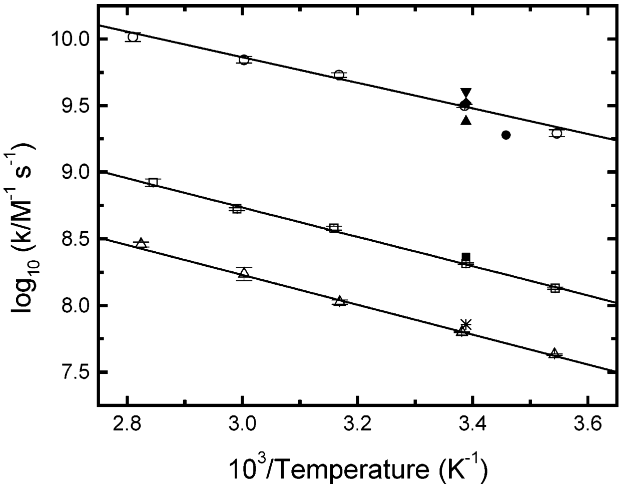

Figure 2. Arrhenius plot of log k vs $1/T$ for aqueous hydrogen atom reaction with SCN^- (□), N_3^- (○), and HN_3 (△). Data points for SCN^- and HN_3 are extrapolated, zero-dose values as shown in Figure 1. Solid lines are weighted linear fits, corresponding to activation energies of 21.1 ± 0.7, 18.4 ± 1.2, and 21.4 ± 0.7 kJ mol^{-1}, respectively. Also shown are previous literature room temperature data for hydrogen atom reaction with SCN^- by Elliot (■);[20] N_3^- by Ye (●, ▲),[24] by Peled (▼),[23] and by Halpern (◆);[21] and HN_3 by Halpern (*).[21]

The measured activation energy of 21.05 ± 0.66 kJ mol^{-1} for SCN^- reaction is similar to some of our previously determined values for other nitrogen-containing compounds listed in Table 1, notably for hydrogen atom reactions with HNO_2/NO_2^- where O-atom abstraction is believed to occur and for N_2H_4 where H-atom abstraction is the dominant pathway. However, having a similar activation energy is not itself a sufficient condition to distinguish between reaction mechanisms, and to maintain consistency with the reported optical absorption data,[20] we believe that the hydrogen atom reaction with SCN^- consists of straightforward adduct formation to give $H(SCN)^{\bullet -}$. As the decay of this species was found not to produce hydrogen gas, Elliot et al. proposed that this transient decays by dissociation of the S−C bond according to the reaction scheme:[20]

$$H(SCN)^{\bullet -} + SCN^- = H(SCN)_2^{2\bullet -} \quad (7)$$

$$\begin{aligned} H(SCN)^{\bullet -} + H^+ &\rightarrow H_2S + CN^{\bullet} + (SCN^-) \\ &\rightarrow CN^- + SCN^{\bullet} \quad (8) \end{aligned}$$

$$H(SCN)_2^{2\bullet -} + H^+ \rightarrow H_2S + CN^- + SCN^{\bullet} \quad (9)$$

to give hydrogen sulfide and cyanide as the final stable products. A search of the literature gave only one other comparable set of data, for the temperature-dependent reaction of the aqueous hydrogen atom with ammonia.[23] However, quantitative comparison to our data was not possible, as the Arrhenius plot for NH_3 reaction ($T = 298-523$ K) was significantly downward curved, with no evident linear region.

Hydrogen Atom Reaction with N_3^-. Comparable measurements were made in this study for the reaction of the hydrogen atom with azide (N_3^-). The pK_a of HN_3 has been measured over the temperature range of 20−33 °C,[22] showing only small changes from its room temperature value of 4.7 at low ionic strength. By assuming that no large deviations occurred at higher temperatures, we were able to measure the reaction of hydrogen atoms with both HN_3 and N_3^- in this study.

The data for the deprotonated N_3^- were collected at pH 9.1 in 0.010 M borate buffer, using N_2O as the saturating gas. Under these conditions, hydrated electrons were quickly converted to hydroxyl radicals, which were then scavenged by reaction with either methanol or azide itself. For the resulting small hydrogen atom concentration, there was no need for dose extrapolations, and so, these data were obtained using only the 55 ns pulse width. These directly measured values are given in Table 2 and are shown in Figure 2. The room temperature reaction rate constant, $k = (3.15 \pm 0.08) \times 10^9$ M^{-1} s^{-1} at 22.2 °C, is seen to be faster than for SCN^- reaction. As a function of temperature, the rate constants for the reaction

$$^{\bullet}H + N_3^- \rightarrow \text{products} \quad (10)$$

were found to be well-described by the equation:

$$\log k_{10} = (12.75 \pm 0.21) - [(18.43 \pm 1.22 \text{ kJ mol}^{-1})/2.303RT] \quad (11)$$

corresponding to an activation energy for this reaction of 18.43 ± 1.22 kJ mol^{-1} (see Table 1).

The rate constant for hydrogen atom reaction with azide has been reported several times previously. Competition kinetic measurements of this room temperature rate constant have been previously performed, using ethanol (3.3×10^9 M^{-1} s^{-1}),[21] 2-propanol (4.0×10^9 M^{-1} s^{-1}),[24] and phenol (2.4×10^9 M^{-1} s^{-1})[25] at pH ~ 7 as standards. One direct EPR measurement[25] has also reported this rate constant as 1.9×10^9 M^{-1} s^{-1} at ~16 °C. These values are shown in comparison to the data of this study in Figure 2; overall, very good agreement is observed.

We believe that reaction 10 results in the formation of the $HN_3^{\bullet-}$ adduct. This transient species has been characterized previously,[26] formed by the reaction of the hydrated electron with HN_3 in aqueous solution. The decay of this transient was found to be first order and dependent upon pH and azide concentration. A general expression for this decay was given as:

$$k_{obs} = 8 \times 10^4 + 3 \times 10^{10}\,[H^+] + 3.3 \times 10^7\,[HN_3]\ s^{-1} \quad (12)$$

Under our experimental conditions, the latter two terms in this expression would be negligible, corresponding to a transient lifetime of ~85 μs.

The authors of ref 26 found that the decay of this transient produced a product that oxidized hydroquinone, *p*-methoxylphenol, *p*-cresol, and *N*,*N*-dimethylamine. They assumed that this species was again $N_3^{\bullet}$, formed by the reaction

$$HN_3^{-\bullet} + H^+ \rightarrow H_2 + N_3^{\bullet} \quad (13)$$

although there was no spectroscopic evidence at short times for the nature of this secondary intermediate. However, this proposed mechanism contradicts the steady-state irradiation finding[21] that H_2 was not a final product of the overall reaction of hydrogen atoms with either N_3^- or HN_3 (see next section). As the rate constant obtained by competition kinetics[21] for hydrogen atom reaction with N_3^- agrees well with the direct EPR measurements of this work and also of Ye et al. (see Figure 2),[25] this indicates that there cannot be any extra H_2 formed from the decay of $HN_3^{-\bullet}$.

To reconcile the finding that another oxidizing transient is produced from the decay of $HN_3^{-\bullet}$ and that H_2 is not a final product, we propose a reaction mechanism analogous to that for SCN^-: that the decay of $HN_3^{-\bullet}$ is instead by proton addition to split a N−N single bond

$$HN_3^{-\bullet} + H^+ \rightarrow NH_2^{\bullet} + N_2 \quad (14)$$

The spectrum of $NH_2^{\bullet}$ has been previously reported,[27] consisting of a single very weak ($\epsilon \sim 80$ M^{-1} cm^{-1}) absorption centered around 525 nm.[28] Unfortunately, we were not able to confirm the formation of this species in subsequent electron pulse radiolysis absorption experiments, due to the low yield of hydrogen atoms under our basic pH conditions. However, the $NH_2^{\bullet}$ radical has been shown to oxidatively react[29] with hydroquinone (pH 11.3; $k = 1.8 \times 10^8$ M^{-1} s^{-1}), *p*-methoxyphenol (pH 11.2; $k = 9 \times 10^6$ M^{-1} s^{-1}), and *p*-cresol (pH 11.2; $k = 4.4 \times 10^6$ M^{-1} s^{-1}), further supporting this alternative reaction mechanism. This alternative mechanism also explains the observed pH and azide concentration dependence (HN_3 can again act as a proton donor, although it would not be significant under our experimental conditions) seen in the kinetics of *p*-benzosemiquinone formation of the previous study.

Hydrogen Atom Reaction with HN_3. For HN_3, kinetic measurements were performed at pH 2.00 over the temperature range of 9.2−81.0 °C. These dose-dependent data were extrapolated as explained previously (see Table 2 for extrapolated limiting rate constants) and are shown in comparison to those of SCN^- and N_3^- in Figure 2. The weighted linear fit to these data gave the temperature-dependent values for the reaction

$$^{\bullet}H + HN_3 \rightarrow \text{products} \quad (15)$$

as

$$k_{15} = (11.59 \pm 0.12) - [(21.44 \pm 0.69\ \text{kJ mol}^{-1})/2.303RT] \quad (16)$$

with a measured activation energy of 21.44 ± 0.69 kJ mol^{-1} (Table 1). Our room-temperature rate constant ($6.31 \pm 0.05 \times 10^7$ M^{-1} s^{-1} at 22.6 °C) agrees reasonably well with the single previous room-temperature competition kinetics measurement of 7.2×10^7 M^{-1} s^{-1} by Halpern and Rabani.[21] This good agreement supports the previous finding that the product of this reaction again is not hydrogen gas, thereby eliminating the expected hydrogen atom abstraction reaction mechanism. By analogy with N_3^-, we propose that the overall reaction mechanism is

$$^{\bullet}H + HN_3 \rightarrow H_2N_3^{\bullet} \quad (17)$$

$$H_2N_3^{\bullet} \rightarrow NH_2^{\bullet} + N_2 \quad (18)$$

This latter mechanism of single N−N bond breakage appears analogous to the one proposed for protonated hydrazine reaction with hydrogen atoms,[10]

$$^{\bullet}H + N_2H_5^{+} \rightarrow {}^{\bullet}NH_2 + NH_3 + H^+ \quad (2)$$

However, although similar products are formed, the large Arrhenius parameters characterizing reaction 2 suggest that significant solvent reorganization and bond breakage has to occur on the way to the transition state.

Acknowledgment. Work described herein at the Radiation Laboratory, University of Notre Dame, was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is contribution no. NDRL-4630 from the Notre Dame Radiation Laboratory. Work performed at Argonne National Laboratory was supported by the U.S. Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under Contract W-31-109-ENG-38.

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