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Temperature Dependence of Hydrogen Atom Reaction with Nitrate and Nitrite Species in Aqueous Solution[†]

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Arrhenius parameters for the reaction of hydrogen atoms with NO_3^-, HNO_2, and NO_2^- in aqueous solution have been determined by the use of pulse radiolysis and electron paramagnetic resonance free induction decay attenuation measurements. At 25.0 °C, the calculated rate constants for these compounds are $(5.61 \pm 0.51) \times 10^6$, $(3.86 \pm 0.09) \times 10^8$, and $(1.62 \pm 0.05) \times 10^9$ dm^3 mol^{-1} s^{-1} respectively, with corresponding activation energies of 48.7 ± 1.0 (15.2−84.5 °C), 21.54 ± 0.69 (5.9−62.8 °C) and 15.59 ± 0.36 (6.2−86.8 °C) kJ mol^{-1}. Computer modeling of these systems suggests that ·H atom reaction with either anion directly produces hydroxide anion and the corresponding NO_x radical.

Introduction

The complex decomposition chemistry of nitrate and nitrite has been investigated for many years, with demonstrated importance in a variety of fields ranging from atmospheric chemistry[1,2] to high-temperature combustion systems.[3] Recent studies have especially illustrated the importance of the radiation-induced decomposition of these two compounds in the nuclear field, where the presence of nitrate, for example, has been proven to influence the rate of molecular hydrogen production in both high level liquid nuclear waste storage[4] and upon the start up of nuclear power reactors.[5]

Despite over 30 years of investigation, there are still many uncertainties in the aqueous radiation chemistry of these two compounds. The hydrated electron has been shown to add to both anions,[6,7] with established room-temperature rate constants of 9.7×10^9 dm^3 mol^{-1} s^{-1} and 3.5×10^9 dm^3 mol^{-1} s^{-1} for nitrate and nitrite, respectively,[8] and the activation energy for nitrate reaction was determined as 16.0 kJ mol^{-1} over the temperature range 283−363 K.[9] Nitrite reaction with the hydroxyl radical occurs with a rate constant of 1.0×10^{10} dm^3 mol^{-1} s^{-1};[10] however, no reaction of this radical with nitrate has been observed.[11] The many investigations of hydrogen atom reaction with these two anions have given a wide range of reported rate constants,[8,12] with all studies performed near room temperature. The one direct electron paramagnetic resonance (EPR) measurement of hydrogen atom reaction rate constants for these two compounds[13] gave a nitrate concentration-dependent rate constant that was much lower than the competition-kinetics values.

In order for the radiation-induced decomposition of nitrate and nitrite to be properly evaluated under the conditions of importance, accurate, temperature-dependent, rate constants for their reaction with all of the primary water radiolysis species need to be known. In this study, we have measured the temperature-dependent rate constants for the reaction of the hydrogen atom with the nitrate and nitrite anions, as well as nitrous acid. Direct EPR detection of the decay of the hydrogen atom following pulse radiolysis was the monitoring method of choice,[14,15] because conventional pulse radiolysis/optical transient absorption methodology is difficult to use given the weak absorption of the reactant and product species at very short wavelengths. The pulsed EPR-based free induction decay (FID) attenuation method[16−20] was used because of the pseudo-first-order scavenging kinetics generally obtained.

Experimental Section

The procedure used for these EPR experiments has been described in detail in several previous publications,[16−20] and thus only a brief description shall be given here. Hydrogen atoms were generated in aqueous solution within an EPR cavity by pulse radiolysis, using 3 MeV electrons from a Van de Graaff accelerator. Stock solutions were prepared by addition of $HClO_4$ (0.10 mol dm^{-3}, Mallinkrodt A. R. Grade, 69.05%) or borax buffer (1.00×10^{-2} mol dm^{-3}, Baker Analyzed) to Millipore-filtered water. Known volumes of this solution were added to the recirculating system, and then de-oxygenated using argon (acid solution) or N_2O (borax buffered). Exact acid concentrations were determined by calculation from standardization of the concentrated acid against 1.029 N HCl (Aldrich, volumetric standard). The solution was flowed through a flat cell in the cavity at a rate sufficient to ensure that each cell volume was completely replaced between pulses. The actual volume irradiated in each pulse was less than 0.10 mL.

The approximate average radiation dose for this cell volume was 1.5, 3.0, and 7.0 krad/pulse for the 12, 25, and 55 ns pulses used, respectively. For extrapolation to obtain the limiting, zero dose, rate constants (see later), the relative dose values used were simply the average beam currents measured on a shutter positioned before the irradiation cell for the three pulse widths. These values were checked frequently to monitor any small drift in the beam. A 35 ns microwave probe pulse was applied to the sample immediately after irradiation, and the resulting free induction decay of the ·H atom low-field ($m_I = {}^1/_2$) EPR transition recorded on a digital oscilloscope. Typically 500−2000 pulses were averaged to measure each FID, at a repetition rate of 120 Hz.

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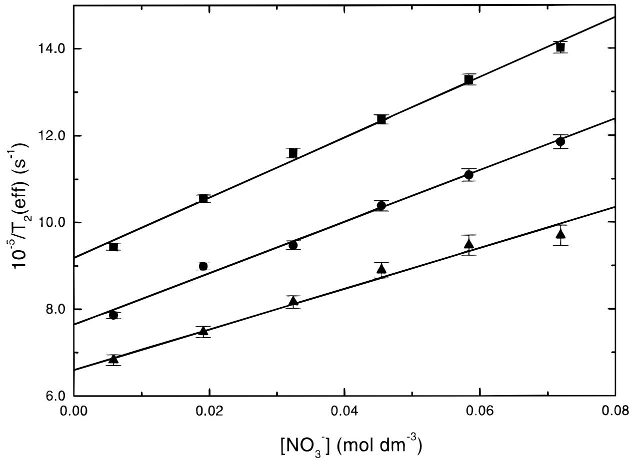

Figure 1. Dose dependence of the aqueous hydrogen atom scavenging rate constant determination for nitrate ion reaction at pH 1.0 and 22.3 °C using the Van de Graaff 55 ns (■), 25 ns (●), and 12 ns (▲) pulse widths. Solid lines are linear fits corresponding to calculated rate constants of (7.13 ± 0.18) × 10^6, (6.04 ± 0.20) × 10^6, and (5.13 ± 0.31) × 10^6 dm^3 mol^{-1} s^{-1}, respectively.

Scavenging experiments were performed by successive injections of concentrated, standard solutions of new KNO_3 (Aldrich, 99.99%) and $NaNO_2$ (Aldrich, 98.8%) to the pH-adjusted stock water. Accuracy of these concentrations is estimated at better than 2%.

All ab initio calculations were carried out using the SPARTAN molecular modelling program of Wavefunction, Inc.[21]

Results

·H Reaction with NO_3^-. The general expression for the effective damping rate of the FID in these experiments is given by[15,18,20]

$$\frac{1}{T_2(\text{eff})} = \frac{1}{T_2^0} + k_s[S] + \sum k_{ex}^i[R_i] \qquad (1)$$

where $k_s[S]$ is the ·H atom scavenging rate and $\sum k_{ex}^i[R_i]$ represents the spin−dephasing contribution of second-order spin exchange and recombination reactions between ·H atoms and other free radicals. At the radiation doses typically used in these experiments the latter term may not be negligible at acid pH's; this effect has been observed previously as a slight dose (pulse width) dependence of the measured scavenging curves.[22−24] The overall hydrogen atom reaction rate constant with the nitrate anion, at pH 1.0 and 22.3 °C,

$$\cdot H + NO_3^- \rightarrow \text{products} \qquad (2)$$

at three different pulse widths (doses) is shown in Figure 1. Although these scavenging plots exhibit excellent linearity the calculated slopes of (5.13 ± 0.31) × 10^6, (6.04 ± 0.20) × 10^6 and (7.13 ± 0.18) × 10^6 dm^3 mol^{-1} s^{-1} for the 12, 25, and 55 ns pulses, respectively, show that such spin exchange does affect the measured rate constants for this system.

To correct the observed rate constants for this dose dependence, limiting values were calculated by extrapolation to zero dose, as shown in Figure 2. An excellent linear relationship was obtained, and for the rate constants listed above a limiting value of (4.44 ± 0.10) × 10^6 dm^3 mol^{-1} s^{-1} was obtained. This procedure was then repeated over the temperature range 15.2−84.5 °C (values for 61.4 °C also shown in Figure 2), with all the extrapolated values given in Table 1 and shown in the Arrhenius plot of Figure 3. Because the pK of HNO_3 is less than −1 over the entire temperature range of measurement,[25] all of the reaction can be attributed to the nitrate anion. From a linear fit to these values, the temperature-dependent rate

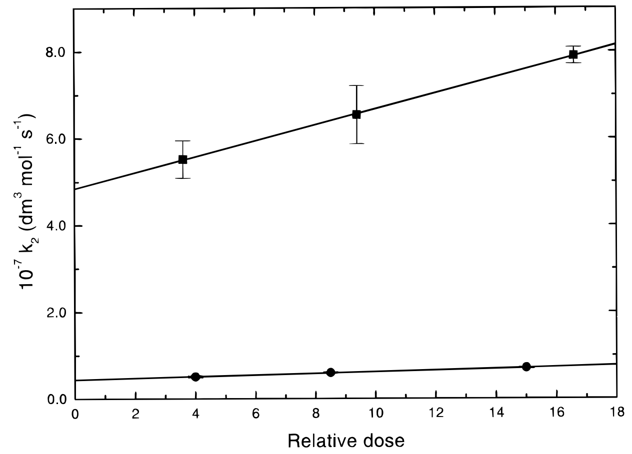

Figure 2. Rate constant extrapolations to zero dose for aqueous hydrogen atom reaction with nitrate at pH 1.0 and 22.3 °C (●) and 61.4 °C (■). Error bars shown correspond to one standard deviation obtained from the linear fit to the FID scavenging plots.

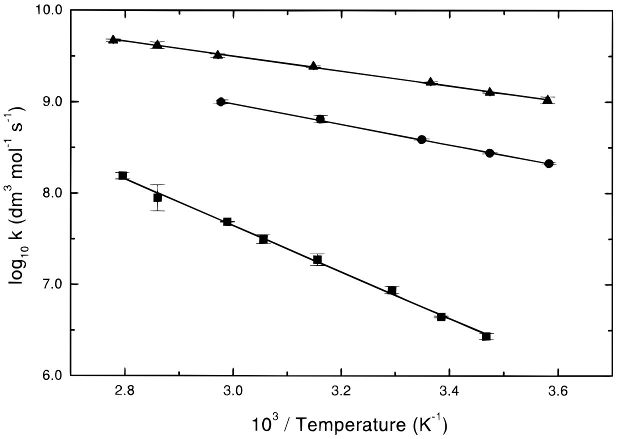

Figure 3. Arrhenius plot of $\log_{10} k_{rxn}$ vs 1/T for aqueous hydrogen atom reaction with NO_3^- (■), HNO_2 (●), and NO_2^- (▲). Solid lines are weighted linear fits, corresponding to activation energies of (48.7 ± 1.0), (21.54 ± 0.69), and (15.59 ± 0.36) kJ mol^{-1}, respectively (see text).

TABLE 1: Summary of the Temperature-Dependent Rate Constant Data for Hydrogen Atom Reaction with NO_3^-, NO_2^-, and HNO_2 in Aqueous Solution

species	temp (°C)	scavenging rate constant (dm^3 mol^{-1} s^{-1})
NO_3^-	15.2	(2.71 ± 0.22) × 10^6
	22.3	(4.44 ± 0.10) × 10^6
	30.4	(8.70 ± 0.81) × 10^6
	43.7	(1.88 ± 0.20) × 10^7
	54.0	(3.15 ± 0.37) × 10^7
	61.4	(4.85 ± 0.04) × 10^7
	76.5	(8.89 ± 3.47) × 10^7
	84.5	(1.55 ± 0.13) × 10^8
HNO_2	5.9	(2.12 ± 0.06) × 10^8
	14.7	(2.76 ± 0.06) × 10^8
	25.4	(3.88 ± 0.07) × 10^8
	43.2	(6.49 ± 0.60) × 10^8
	62.8	(1.00 ± 0.05) × 10^9
NO_2^-	6.2	(1.05 ± 0.09) × 10^9
	14.7	(1.27 ± 0.02) × 10^9
	24.0	(1.64 ± 0.03) × 10^9
	44.5	(2.43 ± 0.05) × 10^9
	63.4	(3.21 ± 0.14) × 10^9
	76.6	(4.15 ± 0.36) × 10^9
	86.8	(4.67 ± 0.16) × 10^9

constants are well described by the expression

$$\log_{10} k_2 = (15.28 \pm 0.16) - [(48700 \pm 1000)/2.303RT] \quad (3)$$

with k_2 and T in units of $dm^3\ mol^{-1}\ s^{-1}$ and K, respectively. This corresponds to an activation energy of 48.7 ± 1.0 kJ mol^{-1}.

There have been many previous investigations of the reaction of the hydrogen atom with the nitrate anion in aqueous solution at room temperature, with rate constants reported over the range $(2.9-40) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ using a variety of competition kinetic systems.[1,26−35] Our room temperature (22.3 °C) value of $(4.44 \pm 0.10) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ is at the low end of this range. There have also been two determinations at lower temperatures. A direct evaluation at 8 ± 2 °C was performed by Smaller et al.,[13] who obtained a concentration-dependent rate constant from the decay characteristics of the ·H atom EPR signal in nitrate solutions, giving an extrapolated rate constant of $k = 1.4 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$. This value is slightly lower than our calculated rate constant of $k_2 = (1.71 \pm 0.18) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$, but there is good agreement within the combined error of the two studies. An earlier determination by Navon and Stein[27] was based on the measurement of total nitrate loss in aqueous solution at 4 °C, due to its reaction with hydrogen radicals created by passing H_2 gas through a discharge system. The rate constants determined by these experiments showed a very strong pH dependence, with calculated values of $(1.15 \pm 0.22) \times 10^7$, $(9.4 \pm 0.3) \times 10^6$, and $(3.8 \pm 1.7) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ for pH's 1−4.7, 7, and 11.6−13.3, respectively. All of these rate constants are much higher than our extrapolated value of $(1.27 \pm 0.13) \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ for this temperature.

·H Reaction with HNO_2. Analogous experiments were performed for nitrite. Because the pK_a of HNO_2 is significantly higher, $pK_a = 3.2$ at 25 °C,[25] both the acid and anion reactions could be separately evaluated.

Because the dose dependence obtained for nitrate was also observed for nitrite, rate constants were again extrapolated to zero dose. The value obtained at pH 1.0 and 25.4 °C by this method for the reaction

$$\cdot H + HNO_2 \rightarrow H_2O + NO \quad (4)$$

was $k_4 = (3.88 \pm 0.07) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$. This rate constant is somewhat lower than the single literature value obtained by ethanol competition kinetics at 26 ± 1 °C of $k = (5.47 \pm 0.26) \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ [36] (allowing for the greater rate constant of hydrogen atom reaction with ethanol[37] at this temperature).

Rate constants were then determined under these conditions over the temperature range 5.9−62.8 °C, with the individual extrapolated values again given in Table 1 and plotted in Figure 3. Experiments at temperatures greater than 63 °C were not reproducible and gave rate constants that were far higher than expected from the extrapolation of lower values in the Arrhenius plot. This behavior is attributed to the known thermal instability of HNO_2 at elevated temperatures.[38] From a linear fit to the measured values, the temperature-dependent rate constant was found to be well described by the expression

$$\log_{10} k_4 = (12.36 \pm 0.12) - [(21540 \pm 690)/2.303RT] \quad (5)$$

corresponding to an activation energy of 21.54 ± 0.69 kJ mol^{-1}. Both the activation energy and preexponential factor are much smaller than determined for nitrate reaction.

There is little doubt that the products of reaction 4 are H_2O and NO as written. In low level ab initio calculations (HF/6-31G**) a transition state for ·H atom reaction at oxygen is found at the large H···OHNO distance of 0.13−0.14 nm.

·H Reaction with NO_2^-. To ensure complete reaction with only NO_2^-, measurements were performed in 1.00×10^{-2} mol dm^{-3} borax buffer, whose temperature dependence has been well characterized.[25] Under these conditions, the hydrogen atom concentration produced was sufficiently low that there was little dose effect; therefore, signals were only obtained using the 55 ns pulse of the Van de Graaff accelerator.

The rate constant measured at pH 9.2 and 24.0 °C by this method for the reaction

$$\cdot H + NO_2^- \rightarrow \text{products} \quad (6)$$

was $k_6 = (1.64 \pm 0.03) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. This value is approximately the average of the reported literature values,[26−28,32,36,39,40] which range from $0.2-2.8 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. The EPR measurements were then repeated over the temperature range 6.2−86.6 °C, with the individual rate constants given in Table 1 and plotted in Figure 3. The temperature dependence for this reaction was found to be well described by the equation

$$\log_{10} k_6 = (11.94 \pm 0.06) - [(15590 \pm 360)/2.303RT] \quad (7)$$

corresponding to an activation energy of 15.59 ± 0.36 kJ mol^{-1}. Again, these Arrhenius parameters are much lower than those determined for the nitrate system.

There has only been one previous determination at lower temperatures, by Smaller et al.[13] who directly measured a rate constant of $k = 7.1 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$ at 281 K. This value is slightly lower than our calculated value of $k_6 = (1.10 \pm 0.04) \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ at this temperature, but again is within the combined errors of the two studies.

Discussion

In previous interpretations of radiation and photochemistry of nitrite and nitrate solutions[6,41−44] it has generally been assumed that ·H atoms would add to the ion, producing the protonated free radical:

$$\cdot H + NO_3^- \rightarrow HNO_3^{\bullet -} \quad (8)$$

$$\cdot H + NO_2^- \rightarrow HNO_2^{\bullet -} \quad (9)$$

Given the reported observation of both of these ion radicals and determination of their pK_a's by transient absorption spectroscopy,[6,41] this was a very reasonable assumption. However, the activation energy of 48.7 ± 1.0 kJ mol^{-1} and preexponential factor of $1.91 \times 10^{15}\ dm^3\ mol^{-1}\ s^{-1}$ found for reaction 2 are both much larger than expected for a simple hydrogen atom reaction. Similar activation energies and preexponential factors have been observed previously for the hydrogen atom reaction with H_5IO_6[45] and $N_2H_5^+$.[46] For the periodic acid complex, the reaction was explained in terms of a concerted oxygen abstraction, dehydration, and iodine complex rearrangement on the basis of the known $\Delta H°$ and $\Delta S°$ of the periodate hydration equilibria. From a similar analysis the hydrogen atom reaction with the acid form of hydrazine was postulated to result in a dissociation of the transition complex to give ammonia, $\cdot NH_2$, and a proton.

In low-level (Hartree-Fock/6-31G* basis) ab initio calculations, reactions 8 and 9 as written are exothermic by some 53.1 kJ, yielding a stable product. However, addition of polarization basis functions (p-type functions on ·H atoms: 6-31G** or 6-311G**) produce dissociation to OH^- and NO or NO_2. For the reaction with nitrite, a transition state is found at an

ONO···H distance of 98 pm. For the reaction with nitrate, the reaction at oxygen is simply downhill, with no transition state. It seems unlikely that any transition state would appear at higher levels of theory, and the high experimental activation energy must correspond to a qualitatively different reaction due to the presence of solvent. Calculations required to investigate specific solvent effects are beyond the scope of this work.

If $HNO_2^{\bullet-}$ and $HNO_3^{\bullet-}$ do exist in the liquid, it must be due to solvent stabilization. We should recall in any case that these radicals and their respective conjugate bases, NO_2^{2-} and NO_3^{2-}, are metastable in water, reportedly dissociating according to reactions 10−13, with the indicated first-order half-lives at room temperature:[6,41]

$$HNO_2^{\bullet-} \rightarrow NO + OH^- \qquad \tau_{1/2} < 12\,\mu s \tag{10}$$

$$NO_2^{2-} + H_2O \rightarrow NO + 2OH^- \qquad \tau_{1/2} = 12\,\mu s \tag{11}$$

$$HNO_3^{\bullet-} \rightarrow NO_2 + OH^- \qquad \tau_{1/2} = 3\,\mu s \tag{12}$$

$$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^- \qquad \tau_{1/2} = 12.5\,\mu s \tag{13}$$

Barker et al.[43] found by conductivity detection of the OH^- product that reaction 13, of NO_3^{2-} with water, was characterized by 49.4 kJ mol^{-1} activation energy and a large preexponential factor of 4.3×10^{13} $dm^3\ mol^{-1}\ s^{-1}$. The activation energy of NO_2^{2-} hydrolysis was much smaller.[43] The similarity of these activation parameters to those found for •H reaction with nitrate and nitrite suggests a commonality of mechanism. If the immediate products (OH^- and NO_2 or NO) of the two reaction sets are the same, the transition states and activation energies might be somewhat similar, even though the reactants appear to be quite different.

According to semiclassical transition state theory (omitting tunneling effects), the Arrhenius preexponential factor corresponds to

$$A = \frac{kT}{h}\exp\left(\frac{\Delta S^{\ddagger}}{R} + 1\right) \tag{14}$$

where $\Delta S^{\ddagger}$ is the activation entropy. Based on this formula, the reaction of the •H atom with NO_3^- must be characterized by a large increase in entropy (+39.2 J mol^{-1} K^{-1}) as the transition state is approached. The entropy change is dominated by changes in low-frequency vibrations and librations and, especially, changes in the hydrogen bonding.

The hydrogen bonding of the nitrate ion has been studied intensely by NMR relaxation methods and infrared spectroscopy.[47] Study of NO_2^- has not been pursued to the same extent. It is generally acknowledged that the nitrate ion is strongly hydrogen bonded to water, and this accounts for its relatively slow rotational relaxation in the plane of the molecule.[47] Likewise, strong hydrogen bonding of the NO_3^{2-} radical to water has been suggested by its EPR relaxation behavior in irradiated nitrate/water glasses.[48] We can speculate that the direct energetically "downhill" attack of the •H atom on the nitrate ion oxygen is prevented by the presence of the hydrogen bonds to surrounding water molecules and that a much higher barrier (perhaps out-of-plane) attack is entropically favored.

It is interesting to consider how the reaction of the NO_3^{2-} radical with water might occur, and what similarity this might have to the reaction of the •H atom with NO_3^-. On the basis of the stoichiometry of reaction 13, two hydroxide ions must be formed. One of these must be formed via proton transfer from a water molecule to the nitrate ion's oxygen. This would apparently lead to the creation of two OH^- ions in contact, but the Grotthus mechanism of proton transfer also allows for transfer via a bridge of H-bonded water molecules,[49,40] and this may provide a more reasonable picture. The only obvious similarity between this proton transfer reaction and the reaction of •H atom with nitrate is the breaking of the N−O bond and formation of $•NO_2$ as a product. The latter aspect of both reactions may be responsible for the positive activation entropies. At least three strong hydrogen bonds to nitrate are broken, giving a large entropy increase. The $•NO_2$ radical is not significantly hydrogen bonded, as indicated by its facile diffusion in ice at low temperatures.[48]

Summary

Arrhenius parameters have been established for aqueous hydrogen atom reaction with the nitrate anion, nitrous acid, and the nitrite anion by direct experimental measurement as

$$\log_{10} k_2 = (15.28 \pm 0.16) - [(48700 \pm 1000)/2.303RT] \tag{3}$$

$$\log_{10} k_4 = (12.36 \pm 0.12) - [(21540 \pm 690)/2.303RT] \tag{5}$$

$$\log_{10} k_6 = (11.94 \pm 0.06) - [(15590 \pm 360)/2.303RT] \tag{7}$$

respectively. On the basis of the Arrhenius parameters for nitrate anion and the results of ab initio computer modeling of this reaction, it is believed that the previously proposed reaction mechanism, consisting of simple addition of the hydrogen atom to produce a metastable radical intermediate, cannot be correct. Rather, the reactions proceed directly to the ultimate OH^- and NO_x products.

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References and Notes

(1) Løgager, T.; Sehested, K. *J. Phys. Chem.* **1993**, *97*, 6664.

(2) Burkholder, J. B.; Mellonki, A.; Ranajit, T.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **1992**, *24*, 711.

(3) Tsang, W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1991**, *20*, 609.

(4) Meisel, D.; Diamond, H.; Horowitz, E. P.; Jonah, C. D.; Matheson, M. S.; Sauer, M. C., Jr.; Sullivan, J. C.; Barnabas, D.; Cerny, E.; Cheng, Y. D. Radiolytic Generation of Gases from Synthetic Waste. Technical Report ANL-91/14; Argonne National Laboratory: Argonne, IL, 1991.

(5) Singh, A.; LeBlanc, J. C. *Use of Gadolinium as a Neutron Absorber in Nuclear Reactors: Radiolysis of Gadolinium Nitrate Solutions*. Technical Report AECL-5526; AECL—Whiteshell Laboratories: Pinawa, MB, Canada, 1976.

(6) Grätzel, M.; Henglein, A.; Taniguchi, S. *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 292.

(7) Kevan, L. In *Radiation Chemistry of Aqueous Systems*; Stein, G., Ed.; Wiley: Chichester, 1968.

(8) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513 and references therein.

(9) Chen, R.; Avotinsh, Y.; Freeman, G. R. *Can. J. Chem.* **1994**, *72*, 1083 and references therein.

(10) Values taken as an average from the reported data in: Barker, G. C.; Fowles, P.; Stringer, B. *Trans. Faraday Soc.* **1970**, *66*, 1509. Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1970**, *92*, 5821. Buxton, G. V. *Trans. Faraday Soc.* **1969**, *65*, 2150. Adams, G. E.; Boag, J. W.; Michael, B. D. *Trans. Faraday Soc.* **1965**, *61*, 1417. Adams, G. E.; Boag, J. W. *Proc. Chem. Soc. London*, **1964**, 112.

(11) Broszkiewicz, R. K. *Int. J. Appl. Radiat. Isot.* **1967**, *18*, 25.

(12) Anbar, M.; Farhataziz; Ross, A. B. Selected Specific Rates of Reactions of Transients from Water in Aqueous Solutions: II. Hydrogen Atom (NSRDS-NBS 51); National Bureau of Standards, U.S. Department of Commerce, U.S. Government Printing Office: Washington, DC, 1975 and references therein.

(13) Smaller, B.; Avery, E. C.; Remko, J. R. *J. Chem. Phys.* **1971**, *55*, 2414.

(14) Fessenden, R. W.; Varma, N. C. *Faraday Discuss. Chem. Soc.* **1977**, *63*, 104.

(15) Bartels, D. M.; Craw, M. T.; Han, P.; Trifunac, A. D. *J. Phys. Chem.* **1989**, *93*, 2412.

(16) Bartels, D. M.; Mezyk, S. P. *J. Phys. Chem.* **1993**, *97*, 4101.

(17) Roduner, E.; Bartels, D. M. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 1037.

(18) Han, P.; Bartels, D. M. *J. Phys. Chem.* **1990**, *94*, 7294.

(19) Han, P.; Bartels, D. M. *Chem. Phys. Lett.* **1989**, *159*, 538.

(20) Han, P.; Bartels, D. M. *J. Phys. Chem.* **1992**, *96*, 4899.

(21) Hehre, W. J.; Huang, W. W. Chemistry with Computation: An introduction to SPARTAN. SPARTAN, version 4.1; Wavefunction, Inc.: Irvine, CA, 1995.

(22) Mezyk, S. P.; Bartels, D. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3127.

(23) Mezyk, S. P.; Bartels, D. M. *Can. J. Chem.* **1994**, *72*, 2516.

(24) Mezyk, S. P.; Bartels, D. M. *J. Phys. Chem.* **1994**, *98*, 10578.

(25) Perrin, D. D. Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution, 2nd ed.; IUPAC Chemical Data Series No. 29; Pergamon Press: New York, 1982.

(26) Appleby, S.; Scholes, G.; Simic, M. *J. Am. Chem. Soc.* **1963**, *85*, 3891.

(27) Navon, G.; Stein, G. *J. Phys. Chem.* **1964**, *69*, 1384.

(28) Hayon, E.; Moreau, M. *J. Chim. Phys.* **1965**, *62*, 391.

(29) Sawai, T. *Bull Chem. Soc. Jpn*, **1966**, *39*, 955.

(30) Chouraqui, M.; Sutton, J. *Trans. Faraday Soc.* **1966**, *62*, 2111.

(31) Airey, P. L.; Dainton, F. S. *Proc. R. Soc. London* **1966**, *A291*, 478.

(32) Anbar, M.; Neta, P. *Int. J. Appl. Radiat. Isotop.* **1967**, *18*, 493.

(33) Volkert, W. A.; Kuntz, R. R. *J. Phys. Chem.* **1968**, *72*, 3394.

(34) Hickel, B., CEA-R-4046, 1970, Saclay, France.

(35) Draganic, Z. D.; Draganic, I. G. *J. Phys. Chem.* **1972**, *76*, 2733.

(36) Halpern, J.; Rabani, J. *J. Am. Chem. Soc.* **1966**, *88*, 699.

(37) Mezyk, S. P.; Bartels, D. M. *J. Phys. Chem.* **1997**, *101*, 1329.

(38) Durrant, P. J.; Durrant, B. *Introduction to Advanced Inorganic Chemistry*, 2nd ed.; J. Wiley and Sons, Inc.: New York, 1970; p 699.

(39) Rabani, J.; Stein, G. *J. Chem. Phys.* **1962**, *37*, 1865.

(40) Sutton, J.; Moreau, M. *Proceedings of the 2nd Tihany Symposium on Radiation Chemistry*; Dobo, J., Hedrig, P., Eds.; Publishing House of the Hungarian Academy of Sciences: Budapest, 1967.

(41) Grätzel, M.; Henglein, A.; Lilie, J.; Beck, G. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 646.

(42) Gonzalez, M. C.; Braun, A. M. *Res. Chem. Intermed.* **1995**, *21*, 837.

(43) Barker, G. C.; Fowles, P.; Stringer, B. *Trans. Faraday Soc.* **1970**, *66*, 1025.

(44) Daniels, M.; Wigg, E. E. *J. Phys. Chem.* **1967**, *71*, 1024.

(45) Mezyk, S. P.; MacFarlane, R.; Bartels, D. M. *J. Phys. Chem.* **1994**, *98*, 12594.

(46) Mezyk, S. P.; Tateishi, M.; MacFarlane, R.; Bartels, D. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2541.

(47) Laaksonen, A.; Kovacs, H. *Can. J. Chem.* **1994**, *72*, 2278 and references therein.

(48) Symons, M. C. R.; Zimmerman, D. N. *J. Chem. Soc., Faraday Trans. I* **1976**, *72*, 409.

(49) Grunwald, E.; Eustace, D. In *Proton Transfer Reactions*; Caldin, E., Gold, V., Eds.; Chapman and Halls Ltd.: London, 1973; p 103.

(50) Bamford, C. H.; Tipper, C. F. H. Proton Transfer. In *Comprehensive Chemical Kinetics*; Elsevier Scientific: New York, 1977; Vol. 8.