Reaction Rate of H Atoms with N₂O in Hot Water

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Abstract

The rate constant of H[•] atoms with N₂O in water has been measured by a competition method up to 300°C. Radiolysis with 2.5MeV electrons generated H[•] atoms, and the HD product from their reaction with deuterated tetrahydrofuran (THF-d₈) was measured with mass spectroscopy. The concentration of THF-d₈ was changed by an order of magnitude in the presence of 25mM N₂O to obtain the ratio of rate constants. To determine the rate constant of H[•] with THF-d₈, a similar competition vs. 0.2mM OH⁻ ion was also measured. The reaction rate of H[•] with OH⁻ has been accurately determined vs. temperature in previous work, allowing the two unknown rate constants to be deduced. Rate constant of H[•] with THF-d₈ follows the Arrhenius law $\ln(k/M^{-1}s^{-1}) = 27.33 - (32.30 \text{ kJ/mol})/RT$. Rate constant of H[•] with N₂O follows the Arrhenius law $\ln(k/M^{-1}s^{-1}) = 24.50 - (30.42 \text{ kJ/mol})/RT$. In all likelihood, the N₂O reaction proceeds via *cis*-HNNO[•] radical intermediate as in the gas phase, but with participation of a bridging water molecule in the 1,3 hydrogen shift to form N₂ and [•]OH products.

Keywords

H atoms; N₂O; radiolysis; water; rate constant; activation energy

1. Introduction

The radiolysis of water by gamma radiation and relativistic electrons is generally described with the chemical equation¹⁻⁵

where the numerical coefficients represent the room temperature yields or G values, defined as the number of species created by 100eV of radiation energy. A widely used trick, apparently first used by Dainton and coworkers^{6,7}, is to saturate the aqueous solution with N₂O gas, which will quickly (within ca. 20ns) convert the solvated electrons to $\cdot\text{OH}$ radicals via overall reaction 2.

The subsequent chemistry is overwhelmingly initiated by the $\cdot\text{OH}$ radicals, and the vast majority of $\cdot\text{OH}$ radical reaction rates and oxidized product radicals have been measured by electron pulse radiolysis using this method⁸. The smaller yield of H $^\bullet$ atoms, ca. 10% of all radicals, is typically ignored. It is generally overlooked that N₂O will also react with the H $^\bullet$ atom, as in Reaction 3.

The rate constant for reaction 2 is $9.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ⁹ while the most recent value for k_3 is $9 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ ¹⁰ at room temperature. The factor of 10^5 difference in rate constants means it is highly likely the H $^\bullet$ atom will react with some impurity or product of radiolysis before it will react with N₂O. Only occasionally is reaction (3) of any importance in room temperature experiments.

N₂O has proven useful as a reagent for capturing solvated electrons in high temperature water as well^{11-14,5}, but it is not obvious whether reaction 3 will remain negligible. A study by Janik, et al ¹⁵ on the rate constant of H• + O₂ in water up to 350 °C demonstrated that at this temperature k_3 is not negligible. A value of $1.25 \pm 0.25 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ was determined for a proper fit of the 350°C data in the 2007 experiment.

The aim of the present study is to determine whether reaction 3 can be described by a simple Arrhenius interpolation between the rate constants already determined at room temperature and at 350°C. Given the relatively slow rate of reaction 3 and the low 25mM solubility of N₂O in water at one atmosphere overpressure, we decided a competition method vs. another slow reaction was likely to give the best results. We have used for some years a high temperature flow system capable of measuring radiolytically generated gases using mass spectroscopic detection¹⁶. With a deuterated scavenger, the specific product HD can be produced from H atoms in a reaction such as (4).

Deuterated tetrahydrofuran (THF-d8) was chosen because it is quite soluble, stable at high temperature¹⁷, and of low cost. The THF-d8 also functions as the scavenger for •OH radicals, via reaction (5)

The HD product resulting from competition between reaction (4) and reaction (3) should be quantitatively described by equation 6,

$$(6)$$

where $[\text{HD}]_0$ is the HD produced in the absence of N_2O . However, k_4 is not yet measured, and so a second competition standard was needed to determine k_4 . The reaction of OH^- ion with $\text{H}^\bullet$, as seen in reaction 7, was selected because the rate constant is well established at high temperature, including all temperatures in this study ^{18,19}.

The experiment is described in the following section. Results are then presented for a modification of the basic competition method, needed to overcome reactions with products. In a Discussion, the results are briefly compared with other measurements and the gas phase reaction.

2. Experimental

The experimental method is described in detail in previous publications ^{16,20}. Briefly, two HPLC pumps were used to generate a total high pressure flow of 6 mL/min. Both pump reservoirs contained the scavenger (OH^- or N_2O), at the same concentration. One reservoir also contained THF-d8 competition partner. The pump flow ratio was changed to achieve the desired THF-d8 concentration. The solution flowed through a pre-heater to reach the desired temperature, at which point it would enter a Hastelloy tube approximately 3 cm in length. The sample was irradiated from the side with a 2.5 MeV electron beam whilst moving through this tube. Upon exiting, the solution flowed through a cooling bath and a capillary, where the pressure dropped back to ambient. A precise sample volume of 18 to 60ml was collected in a glass vessel. The sample volume was sparged with ultra high purity argon, and HD, H_2 , N_2 , and in some cases O_2 were detected

using mass spectroscopy. The measured HD peaks were integrated to determine the concentration assuming the same calibration as was determined for H₂ concentration.

THF-d8 (Sigma-Aldrich, 99.5% d) concentration was varied during the experiment from a maximum of 24.6 mM to a minimum of 1.2 mM. The competition between Reactions 3 and 4 used a constant concentration of 25 mM N₂O (Airgas analytical grade). The competition between Equations 4 and 7 used constant 0.2 mM NaOH prepared from Fluka Analytical 0.1 M standard NaOH solution. In the latter experiments, 0.5 mM N₂O (Airgas 2% N₂O in Argon) was also added in both reservoirs to scavenge (e⁻)_{aq} generated in Reaction 7. Doses in the range of approximately 40-800 Gy were used. This range was chosen as it ensured that N₂O and THF-d8 were not depleted to the point where a pseudo-first order kinetics analysis is no longer valid.

Absolute dosimetry was not generally measured on each day. The H₂ signal was measured along with HD in every experiment, and used as an approximate internal dosimeter. This works well for the OH⁻ experiment, but 25mM N₂O is enough to perturb the G values for both H and H₂. Moreover, the sensitivity for HD is only approximately identical to that for H₂. In the analysis presented below, only the relative dose for various experiments is required, and this is given very accurately by the electron beam current and the H₂ signals in a given run.

3. Results and Discussion

The standard competition Equation 6 is derived based on the assumption that in absence of another scavenger, all H atoms will react with THF-d8 to produce HD. However, preliminary investigation (with low N₂O concentration) revealed the amount of

HD produced at elevated temperature was significantly smaller than expected, and not linear vs. the applied dose, even though signals of N₂ and H₂ are quite linear, with zero intercept. The THF is a thermally stable compound^{17 21} and routine measurements of blank (non- irradiated) samples did not show up any signs of thermal degradation of THF in the whole range of studied temperatures. The gas analysis of THF samples irradiated above 100 °C showed additional signal with mass 28. The signal can be assigned to carbon monoxide which must be generated from thermal decomposition of a radiolytically generated product of THF, perhaps on the flow system walls.

In general carbon-centered radicals such as $\cdot\text{THF-d7}$ will recombine to form a C-C bonded dimer, but it is also very common that they produce an unsaturated product (call it u-THF-d6) via H $\cdot$ (or D $\cdot$ in this case) atom transfer disproportionation²²:

The hydrogen atom would much more readily add to the double bond of the unsaturated product as in reaction 9 (rate constant ca. $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at room temperature based on similar compounds^{8,23}) than it would participate in the deuterium abstraction to form HD shown in Equation 4:

We postulate that the "missing" signal and nonlinearity of [HD] vs. dose is due to reaction (9) at high temperature.

All primary radicals are expected to produce $\cdot\text{THF-d7}$ via reactions (4) and (5) regardless of the THF-d8 concentration in our experiment. Virtually all of these $\cdot\text{THF-d7}$ radicals are expected to self-recombine, some fraction via disproportionation reaction (8).

Consequently, for a given dose rate, we expect the same growth of unsaturated product u-THF-d6 regardless of the initial THF-d8 concentration. As long as sufficient product is formed relative to its consumption by the $H^\bullet$ atom reaction, we can treat reaction (9) as an additional pseudo-first-order loss channel, and modify equation 6 as

$$(10)$$

where it is understood that $[u\text{-THF-d6}]$ represents an average concentration over the period of irradiation. Equation (10) can be linearized in the form

$$(11)$$

Figure (1) demonstrates that a plot of $1/[HD]$ vs. $1/[THF-d8]$ gives very linear behavior for three different doses at room temperature, and similar plots for all of the experiments are shown in Supporting Information. According to equation (11) the ratio of slope to intercept at each particular dose gives the relation

$$[12]$$

The quantity $[u\text{-THF-d6}]$ represents the average unsaturated product concentration during the experiment. According to the assumption that all of the $\bullet\text{THF-d7}$ radicals self-recombine, this average product concentration is simply proportional to the dose. It follows that if we plot slope/intercept vs. (relative) dose, and extrapolate to zero dose, the intercept of this dose plot will be $k_3[N_2O]/k_4$, from which we can calculate k_3/k_4 as originally intended. Plots of data for the N_2O vs. THF-d8 competition at 25, 100, 200, and 300°C are shown in Supporting Information figures S1-S4.

The kinetics equations 10-12 are explicitly written for the competition between N_2O and THF-d8. The analysis for the competition between OH^- and THF-d8 is

identical, except $k_3[\text{N}_2\text{O}]$ must be substituted with $k_7[\text{OH}^-]$. Data plots for this competition at 25, 100, 200, and 300°C are shown in Supporting Information figures S5-S8. Under the optimized conditions of the final experiments, there is virtually no effect of the unsaturated product (i.e. dose effect) at 25°C, but there is a significant correction at higher temperatures.

Figure 1. Competition plots for $\text{H}^\bullet$ with OH^- vs THF-d8 for three different doses at 25 °C.

Figure 2. Plot of slope/intercept (equation 11) as a function of dose in Gy. The intercept is used to determine the rate constant ratios. The black solid lines are for the competition between THF-d8+H• and OH•+H• at 25°C (left graph) and 200 °C (right graph). The red dotted lines are for the competition between THF-d8+H• and N₂O+H• respectively at 25°C (left) and 200 °C (right).

A summary of the measured rate constant ratios can be found in Table 1. The ratios were used to determine unknown rate constants k_3 and k_4 by using the values of k_7 found in references ¹⁸ and ¹⁹. An Arrhenius plot for k_4 is found in figure 3, and for k_3 is found in figure 4. Approximate linearity within the error bars is found for both reactions. Arrhenius parameters are given in Table 2. Both reactions have activation energy close to 30 kJ/mole. As expected, the Arrhenius parameters for reaction 4 are nearly identical to the similar deuterium abstractions from ethanol-d5 and propanol-d7.²⁴

Table 1. Summarized rate constants for reactions 3, 4, and 7.					
Temperatur e (°C)	^{a,b} k_7 ± 10%	k_7/k_4	k_4	k_4/k_3	k_3
25		14.7		8.17	
100		9.20		14.3	
200		13.8		12.4	
300		10.8		7.44	

a)¹⁹; b)¹⁸

Table 2: Arrhenius activation energies and pre-exponentials from Figs. 3 and 4.

Reaction	Activation Energy (kJ)	Pre-Exponential (M ⁻¹ s ⁻¹)
THF-d8+H• → •THF-d7+HD	32.3 ± 1.2	
N ₂ O+H• → N ₂ +•OH	30.4 ± 2.1	

Errors for the raw data points are estimated from the noise in the mass spec baselines and signal amplitudes, and are generally below 5%. At lower dose, the smaller [HD] generated can be compensated by collecting a larger quantity of water. Standard errors of the slope and intercept for linear scavenging plots are estimated in the usual way. Propagation of the standard errors in each subsequent algebraic manipulation is carried out by calculation of the RMS sum of the relative standard errors. The final results in Table 1 are reported with 90% confidence intervals, using the computed standard errors and the Student t-distribution appropriate for the number of observations minus the number of degrees of freedom.²⁵ The uncertainty of the standard reaction rate k_7 is not included in this calculation.

Figure 3. Arrhenius plot for the rate constant of THF-d8 + H•

Figure 4. Arrhenius plot for the rate constant of N₂O + H•. The line fits only the experimental data determined in this study.

4. Discussion

We have resolved the question initially posed in our study. The rate constant of reaction 3 between N_2O and $\text{H}^\bullet$ follows Arrhenius behaviour in water up to 350 °C, and the measurement of Janik, et al¹⁵ at 350°C lies perfectly on the plot. Our rate constant at 25 °C of $(2.0 \pm 0.4) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ is twice the number $(9 \pm 2) \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ reported recently by Kazmierczak, et al¹⁰, but is much less than $2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ provided by Czapski and Peled²⁶. The latter number is the only one found in the comprehensive rate constant review of Buxton, et al,⁸ and so it has been the most widely used in recent years. It is certainly justified to ignore reaction 3 at room temperature in most studies. This may also be justified at high temperature depending on the application, but now that we have provided the data, one can make a correction as needed up to 350°C.

It is interesting to compare the rate constant for reaction 3 in water with the gas phase high pressure limit. The gas phase mechanism and rate of reaction 3 has been studied for decades due to its importance in combustion processes²⁷⁻³⁰. Two reaction channels have been identified. The first is a "direct" attack of the $\text{H}^\bullet$ atom at the oxygen end of the N_2O molecule, giving the N_2 and $\bullet\text{OH}$ product. The second "indirect" mechanism involves addition of the $\text{H}^\bullet$ atom at the nitrogen end, producing a stable *cis*- $\text{HNNO}^\bullet$ radical intermediate. This intermediate rearranges via a 1,3-hydrogen shift, breaking the N-O bond in the process and leading again to the stable N_2 and $\bullet\text{OH}$ products. According to the high level QCISD(T)/cc-pvTZ calculations of Castillo, et al, the direct attack at oxygen is characterized by an activation enthalpy of 88 kJ/mole,

whereas the addition at nitrogen has activation enthalpy of 52 kJ/mole³⁰. The *cis*-HNNO[•] intermediate is stabilized by -56 kJ/mole relative to reactants (but still 228 kJ/mole above the N₂ and [•]OH product). The highly strained transition state for the 1,3-hydrogen shift lies at 80 kJ/mole above the reactants and 136 kJ/mole above the *cis*-HNNO[•] intermediate. In the gas phase, the reaction rates are also complicated by tunneling effects. The general picture seems to be that in high temperature flames, the direct attack at oxygen is favored, but at lower temperatures the indirect mechanism dominates.

It is not immediately obvious how we can arrive at a 30 kJ/mole activation energy for reaction 3 in water given the much higher activation barriers in the gas phase. Tunneling effects are generally quenched in liquid water, and this tends to produce a larger activation energy in water than might be present in the gas phase³¹⁻³³. The H[•] atom is hydrophobic, characterized by a positive solvation free energy in water³⁴. In general this unfavorable free energy may be "recovered" in the transition state, producing a "hydrophobic acceleration" of the reaction rate relative to the gas phase^{35,36}. The acceleration is diminished at higher temperature, and so the overall effect may reduce the activation energy in water by a few kJ/mole. It is similarly plausible that the transition states of either pathway may be stabilized, relative to the gas phase, by nonspecific solvation of the dipole moments. This should not amount to more than a few kJ/mole.

Given the very high gas phase barrier for the direct attack at oxygen³⁰, it is difficult for us to imagine that this pathway contributes to the reaction in water. It is plausible, with favorable solvation of the transition state, that the 52 kJ/mole activation enthalpy for the formation of *cis*-HNNO[•] might be lowered to the observed 30 kJ/mole

activation energy in water. This does not resolve our problem, however, because the gas phase barrier for the 1,3 hydrogen shift remains much higher. If this second barrier remains high, we would merely establish a pre-equilibrium and the observed reaction rate would be given by $k_3 = K_{eq} k_f$, where K_{eq} is the equilibrium constant for forming *cis*-HNNO* from reactants, and k_f is the forward reaction rate to products. The large activation energy of the 1,3-hydrogen shift would dominate. To resolve this problem, we propose that the 1,3-hydrogen shift is replaced in liquid water by a Grotthus-type relay mechanism involving a bridging water molecule, such that the proton transfers from HNNO* to the water oxygen, and simultaneously another proton transfers from this water to the HNNO* oxygen. The six-member ring of this configuration should relieve the geometrical strain of the nearly square gas phase transition state, and might greatly reduce the activation energy. We leave the verification of this explanation to others more interested to carry out the necessary calculations.

At the stage of final acceptance for this manuscript we became aware of new work by Kazmierczak, et al , reporting aqueous phase rate constants for reaction 3 up to 70°C.³⁷ The activation energy is reported as 62.6 kJ/mole, with Arrhenius pre-exponential of $8.2 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$. They compare this activation energy with ab initio calculations in the literature and additional calculations in dielectric continuum "solvent", and conclude the direct attack of H atom at the oxygen atom of N₂O is the preferred mechanism in solution. Obviously this conclusion is directly opposite to our own. Their conclusion is understandable on the basis of their activation energy, but no comment at all was made regarding the astonishingly large pre-exponential factor in their report. In our

opinion no mechanistic conclusion should be accepted without an explanation of the large positive activation entropy that this pre-exponential implies.

The Arrhenius dependence reported by Kazmierczak, et al,³⁷ if extrapolated to 100°C, would predict a rate constant 3.7 times larger than our measurement in Table 1. If extrapolated to 350°C, their equation would produce a rate constant of $4.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and a chemical lifetime for the H[•] atom in 25 mM N₂O solution of only one nanosecond. The experimental results of Janik, et al¹⁵ would be impossible to obtain with this activation energy, as would the HD product measurements at 200°C and 300°C of the present work.

The transient optical method adopted by Kazmierczak, et al³⁷ amounts to a competition of the pseudo-first-order reaction 3 against the second order recombination of Cl₂^{•-} radical with itself and with H[•] atoms. The temperature dependence of several second order reaction rates, radiation yields and extinction coefficients must be precisely known in order to extract the desired information from fitting a system of partial differential equations. Once this data is collected, and assuming the mechanism is complete, there is no reason that the experiment should give a wrong answer. However, we believe that somehow a systematic error entered into the work of Kazmierczak, et al³⁷, and lead them to an erroneous conclusion regarding the mechanism of reaction 3.

Acknowledgement

This work was supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through award DE-FC02-04ER15533. This is manuscript number 5149 of the Notre Dame Radiation Laboratory.

References

- (1) Draganic, I. G.; Draganic, Z. D. *The Radiation Chemistry of Water*; Academic Press: New York, 1971.
- (2) Buxton, G. V. Radiation Chemistry of the Liquid State: (1) Water and Homogeneous Liquid Solutions. In *Radiation Chemistry. Principles and Applications*; Farhataziz, Rodgers, M. A. J., Eds.; VCH Publishers: New York, 1987.
- (3) Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry, 3rd Edition*; Wiley Interscience: New York, 1990.
- (4) Elliot, A. J.; Bartels, D. M. "The Reaction Set, Rate Constants and g-Values for the Simulation of the Radiolysis of Light Water over the Range 20° to 350°C Based on Information Available in 2008", report AECL 153-127160-450-001, Atomic Energy of Canada, Ltd., 2009.
- (5) Sterniczuk, M.; Yakabuskie, P. A.; Wren, J. C.; Jacob, J. A.; Bartels, D. M. Low LET radiolysis escape yields for reducing radicals and H₂ in pressurized high temperature water. *Radiat. Phys. Chem.* **2016**, *121*, 35-42.
- (6) Dainton, F. S.; Peterson, D. B. Use of Nitrous Oxide to Discriminate Between the Forms of Hydrogen Atoms (H⁰ and H₂⁺ ?) Produced by Gamma-Irradiation of Aqueous Solutions. *Nature* **1960**, *186*, 878-879.
- (7) Dainton, F. S.; Peterson, D. B. Forms of H and OH Produced in Radiolysis of Aqueous Systems. *Proceedings of the Royal Society of London Series a-Mathematical and Physical Sciences* **1962**, *267*, 443-&.
- (8) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical-Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen-Atoms and Hydroxyl Radicals (·OH/O·) in Aqueous-Solution. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513-886.
- (9) Elliot, A. J. A pulse radiolysis study of the temperature dependence of reactions involving H, OH and e_{aq}⁻ in aqueous solutions. *Radiat. Phys. Chem.* **1989**, *34*, 753-758.
- (10) Kazmierczak, L.; Swiatla-Wojcik, D.; Szala-Bilnik, J.; Wolszczak, M. Rate of reaction of the hydrogen atom with nitrous oxide in ambient water. *Radiat Phys Chem* **2016**, *125*, 156-159.

- (11) Takahashi, K. J.; Ohgami, S.; Koyama, Y.; Sawamura, S.; Marin, T. W.; Bartels, D. M.; Jonah, C. D. Reaction Rates of the Hydrated Electron with N₂O in High Temperature Water and Potential Surface of the N₂O- Anion. *Chem. Phys. Lett.* **2004**, *383*, 445-450.
- (12) Bonin, J.; Janik, I.; Janik, D.; Bartels, D. M. Reaction of the Hydroxyl Radical with Phenol up to Supercritical Conditions. *J. Phys. Chem. A* **2007**, *111*, 1869-1878.
- (13) Janik, I.; Bartels, D. M.; Jonah, C. D. Hydroxyl Radical Self-Recombination Reaction and Absorption Spectrum in Water up to 350°C. *J. Phys. Chem. A* **2007**, *111*, 1835-1843.
- (14) Kanjana, K.; Walker, J. A.; Bartels, D. M. Hydroxymethyl Radical Self-Recombination in High-Temperature Water. *J. Phys. Chem. A* **2015**, *119*, 1830-1837.
- (15) Janik, I.; Bartels, D. M.; Marin, T. W.; Jonah, C. D. Reaction of O₂ with the hydrogen atom in water up to 350 degrees C. *J Phys Chem A* **2007**, *111*, 79-88.
- (16) Janik, D.; Janik, I.; Bartels, D. M. Neutron and beta/gamma radiolysis of water up to supercritical conditions. 1. beta/gamma yields for H₂, H[•] atom, and hydrated electron. *J Phys Chem A* **2007**, *111*, 7777-7786.
- (17) Richter, T.; Vogel, H. The dehydration of 1,4-butanediol to tetrahydrofuran in supercritical water. *Chemical Engineering & Technology* **2001**, *24*, 340-343.
- (18) Han, P.; Bartels, D. M. H/D Isotope Effects in Water Radiolysis .4. The Mechanism of (H)_{aq} <=>(e⁻)_{aq} Interconversion. *J. Phys. Chem.* **1992**, *96*, 4899-4906.
- (19) Marin, T. W.; Jonah, C. D.; Bartels, D. M. Reaction of Hydrogen Atoms with Hydroxide Ions in High-Temperature and High-Pressure Water. *J. Phys. Chem. A* **2005**, *109*, 1843-1848.
- (20) Sterniczuk, M.; Bartels, D. M. Source of Molecular Hydrogen in High-Temperature Water Radiolysis. *J Phys Chem A* **2016**, *120*, 200-209.
- (21) Klute, C. H.; Walters, W. D. The Thermal Decomposition of Tetrahydrofuran. *J Am Chem Soc* **1946**, *68*, 506-511.
- (22) Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry: Structure and Mechanism*; Cambridge University Press: Cambridge, 1974.

- (23) Madden, K. P.; Mezyk, S. P. Critical Review of Aqueous Solution Reaction Rate Constants for Hydrogen Atoms. *J. Phys. Chem. Ref. Data* **2011**, *40*.
- (24) Mezyk, S. P.; Bartels, D. M. Rate of hydrogen atom reaction with ethanol, ethanol-d(5), 2-propanol, and 2-propanol-d(7) in aqueous solution. *J. Phys. Chem. A* **1997**, *101*, 1329-1333.
- (25) Peters, D. G.; Hayes, J. M.; Hieftje, G. M. *Chemical Separations and Measurements. Theory and Practice of Analytical Chemistry*; W. B. Saunders Company: Philadelphia, 1974.
- (26) Czapski, G.; Peled, E. On the pH-dependence of G-reducing in the radiation chemistry of aqueous solutions. *Isr. J. Chem.* **1968**, *6*, 421-436.
- (27) Marshall, P.; Fontijn, A.; Melius, C. F. High-Temperature Photochemistry and BAC-MP4 Studies of the Reaction Between Ground-State H-atoms and N₂O. *J. Chem. Phys.* **1987**, *86*, 5540-5549.
- (28) Walch, S. P. Theoretical Characterization of the Potential-Energy Surface for NH+NO. *J. Chem. Phys.* **1993**, *98*, 1170-1177.
- (29) Castillo, J. F.; Collins, M. A.; Aoiz, F. J.; Banares, L. Quasiclassical trajectory study of the dynamics of the H+N₂O reaction on a new potential energy surface. *J. Chem. Phys.* **2003**, *118*, 7303-7312.
- (30) Castillo, J. F.; Aoiz, F. J.; Banares, L.; Collins, M. A. The H+N₂O → OH+N₂ reaction dynamics on an interpolated QCISD potential energy surface. A quasiclassical trajectory study. *J. Phys. Chem. A* **2004**, *108*, 6611-6623.
- (31) Schenter, G. K.; McRae, R. P.; Garrett, B. C. Dynamic Solvent Effects on Activated Chemical-Reactions .1. Classical Effects of Reaction-Path Curvature. *J. Chem. Phys.* **1992**, *97*, 9116-9137.
- (32) Truhlar, D. G.; Schenter, G. K.; Garrett, B. C. Inclusion of Nonequilibrium Continuum Solvation Effects in Variational Transition-State Theory. *Journal of Chemical Physics* **1993**, *98*, 5756-5770.
- (33) McRae, R. P.; Schenter, G. K.; Garrett, B. C. Dynamic solvent effects on activated chemical reactions .2. Quantum mechanical effects. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 997-1009.

- (34) Roduner, E. Hydrophobic Solvation, Quantum Nature, and Diffusion of Atomic Hydrogen in Liquid Water. *Radiat. Phys. Chem.* **2005**, 72, 201-206.
- (35) Roduner, E.; Bartels, D. M. Solvent and Isotope Effects on Addition of Atomic-Hydrogen to Benzene in Aqueous-Solution. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1992**, 96, 1037-1042.
- (36) Marin, T. W.; Jonah, C. D.; Bartels, D. M. Reaction of OH⁻ Radicals with H₂ in Sub-Critical Water. *Chem. Phys. Lett.* **2003**, 371, 144-149.
- (37) Kazmierczak, L.; Swiatla-Wojcik, D.; Wolszczak, M. Reaction of the hydrogen atom with nitrous oxide in aqueous solution - pulse radiolysis and theoretical study. *RSC Advances* **2017**, 7, 8800-8807.