THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 107, NUMBER 17, MAY 1, 2003

LETTERS

Prediction of Rate Constants for Reactions of the Hydroxyl Radical in Water at High Temperatures and Pressures

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Received: December 30, 2002; In Final Form: March 17, 2003

There is a need for accurate data on the rate constants of many reactions involved in the radiolysis of water at high temperature and pressure, to model aqueous chemistry in the heat transport systems of water-cooled nuclear reactors. Given the absence of direct experimental data, it is usual to extrapolate rate constants from lower temperature measurements. However, recent studies of muonium kinetics show that rate constants go through a maximum and fall with temperature under near critical and supercritical conditions. This behavior can be explained by the cage effect, in particular the number of collisions between a pair of reactants over the duration of their encounter. The model developed for reactions of muonium is equally valid for fast reactions in the radiolysis of water. It is used here to estimate the rate constants of near diffusion-controlled reactions of hydroxyl radicals in sub- and supercritical water. The results show significant differences from literature values commonly used to model aqueous radiation chemistry in nuclear reactors. In view of this, it is recommended that the predictions of earlier models be reconsidered.

I. Introduction

Accurate modeling of aqueous chemistry in the heat transport systems of pressurized water-cooled nuclear reactors (PWRs) requires data on the rate constants of many reactions involved in the radiolysis of water.[1−4] Unfortunately, available experimental data do not extend to the high temperatures used in current PWRs, typically around 300 °C; future designs employ even higher temperatures,[5,6] above the critical point of water (374 °C, 220 bar). Thus, the practice of extrapolating experimental data on diffusion coefficients and rate constants from their measured ranges (mostly less than 200 °C) should be viewed with caution.

Because the free radical reactions involved in the radiolysis of water are generally very fast, close to the diffusion limit at room temperature, it is common practice[1,3,4] to employ the Noyes equation[7] to rationalize the temperature dependence of the rate constants

$$1/k_{\text{obs}} = 1/k_{\text{diff}} + 1/k_{\text{act}} \tag{1}$$

The Schmoluchowski equation relates the diffusion-limited rate constant k_{diff} to the diffusion constants D_i of the reactants and their mutual reaction diameter R_{eff}

$$k_{\text{diff}} = 4000\pi\beta(D_1 + D_2)R_{\text{eff}}\,N_{\text{Av}} \tag{2}$$

where β is the spin statistical factor for reactions between radicals, and the factor $1000N_{\text{Av}}$ serves to express the rate constant in conventional chemical kinetics units, $M^{-1}\ s^{-1}$. Equation 2 must be modified by a factor 0.5 if the two reactants are identical and by the Debye factor if both are charged. Thee

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10.1021/jp027858q CCC: $25.00

rate constant for activation control k_{act} is usually represented by a simple Arrhenius expression

$$k_{act} = A \exp(-E_a/RT) \tag{3}$$

Equations 1−3 have been used to fit kinetic data from a wide range of reactions involving radiolysis transients.[8−10] This procedure is generally very successful for describing data empirically, but one should question the validity of extrapolation outside the temperature range of measurements when the fit parameters do not have meaningful values. Almost all of the reactions studied exhibit convex Arrhenius plots, and this is nicely explained by a gradual shift from diffusion control to activated reaction with E_a lower than the effective activation energy for diffusion. However, some reactions can only be characterized with negative activation energies E_a. Such behavior is particularly prevalent for reactions of hydrated electrons and has been explained by reversible electron transfer.[11] On the other hand, such abnormal temperature dependence is not restricted to reactions of the hydrated electron, and this is becoming more evident as kinetics measurements are extended to higher temperatures.

Our own experience with measurements of muonium kinetics in sub- and supercritical water[12−14] suggests that the existence of curvature and even a maximum in the rate constant as a function of temperature may be a general phenomenon. We have observed such behavior for a wide range of reactions of muonium: spin exchange, addition to aromatic molecules, H atom abstraction, and muon transfer. We concluded that a key factor in the temperature dependence of bimolecular rate constants at high temperature is the cage effect, in particular the number of collisions between a pair of reactants over the duration of their encounter.[12]

Because muonium (Mu) is chemically equivalent to the H atom and is even considered a light isotope of that element, our findings for Mu should apply equally well to H. Furthermore, our model for Mu reaction kinetics may be extended to the reactions of other small hydrophobic radical species. In this paper, we apply our model to literature data, taking as examples some reactions of the hydroxyl radical.

II. Computational Model

Our "multiple collisions" model is described in detail elsewhere[12,13] and is only summarized here. It makes use of the Noyes formulation, eq 1, for combining the effects of diffusion and reaction, but eq 3 is modified to include an efficiency factor f_R

$$k_{react} = f_R A \exp(-E_a/RT) \tag{4}$$

$$f_R = p_R q/(1 + p_R q) \tag{5}$$

which takes account of both the reactive orientation (factor p_R) and q the number of collisions between the reactants over the duration of an encounter. The latter can be expressed as the ratio of the encounter lifetime and the time between collisions

$$q = \tau_{enc}/\tau_{coll} \tag{6}$$

Approximate fomulae for estimating these times can be found elsewhere.[12,13] What is important is that q for small reactants typically falls from 10^3 collisions per encounter in liquid water at low temperature to single-collision, gaslike behavior under low-density supercritical conditions. Thus, the reaction efficiency falls from 100% per encounter in high-density water to some lower value determined by the orientation factor p_R.

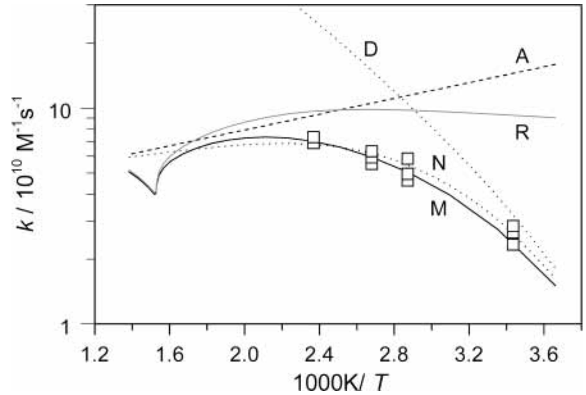

Figure 1. Arrhenius plot of the rate constant for the reaction of the hydroxyl radical with the hydrated electron in water. The experimental data (squares) are taken from ref 15. The dotted lines denote analysis by the method of Elliot et al.,[8−10] which employs the Noyes equation (line N, eq 1) to combine the diffusion-limited rate constant (line D, eq 2) and the Arrhenius expression for an activated reaction (line A, eq 3). The positive slope of line A comes from the negative value used by Elliot et al. for the activation energy. Line M denotes the prediction of the multiple-collisions model,[12,13] using the same diffusion parameters as Elliot et al. but a modified expression for the activation-controlled rate constant (line R, eq 4), with $A = 1.4 \times 10^{11}$ M^{-1} s^{-1}, $E_a = 1$ kJ mol^{-1}, $p_R = 1.0$.

The parameters of the multiple collisions model include the temperature dependent properties of water (density and viscosity) and various reactant characteristics (diffusion constants and reaction diameters). If one uses literature data for such solvent and reactant properties, there remain only three empirical variables: A, E_a, and p_R.

III. Reactions of the Hydroxyl Radical

The reaction between the hydrated electron and the hydroxyl radical is a key step in the radiolysis of water, being the main pathway for reforming water molecules in the spur[15]

$$e_{aq}^- + OH \rightarrow OH^- \tag{7}$$

It is a typical example of a reaction which appears to have a negative activation energy according to the widely used kinetic analysis of Elliot et al.[8−10] Their approach is demonstrated with the dotted lines labeled D (diffusion), A (Arrhenius), and N (Noyes) in Figure 1. Also plotted is an alternative analysis based on our multiple collisions model: lines D, R, and M. To allow direct comparison with the earlier work, we have employed exactly the same diffusion parameters (hence line D) and set $p_R = 1$. Similarly, following the practice of Elliot et al.,[8,9] we have set the spin statistical factor β to 1.0 for radical−radical reactions involving OH. Thus, only two empirical variables remain; lines R and M arise from $A = 1.4 \times 10^{11}$ M^{-1} s^{-1} and $E_a = 1$ kJ mol^{-1} (compared with $A = 3.4 \times 10^{10}$ M^{-1} s^{-1} and $E_a = -3.5$ kJ mol^{-1} for lines A and N).

Both lines N and M exhibit curvature, and extrapolation to higher temperature predicts a broad maximum in both cases. The main difference is the dip in M close to the critical temperature. The dip is less pronounced at higher pressure (line M corresponds to a pressure of 240 bar) but deepens for $p_R < 1$. However, the experimental data is inadequate to choose between the two extrapolations.

The effect of pressure and the orientation parameter p_R are demonstrated in Figure 2, which displays data[16] and model

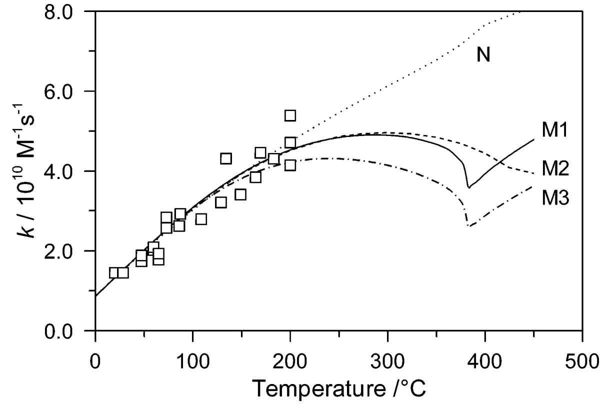

Figure 2. Temperature dependence of the rate constant for the reaction of the hydroxyl radical with the H atom in water. The experimental data (squares) are taken from ref 16. The dotted line (N) shows the fit and extrapolation used by Elliot. The three lines M1, M2, and M3 are examples of predictions using the multiple collisions model. They use the same diffusion parameters as N and have common activation parameters ($A = 2.2 \times 10^{11}$ M^{-1} s^{-1}, $E_a = 5$ kJ mol^{-1}). The only difference is in pressure (240 bar for M1 and M3, 400 bar for M2) and orientation parameter (p_R is 1.0 for M1 and M2 and 0.6 for M3).

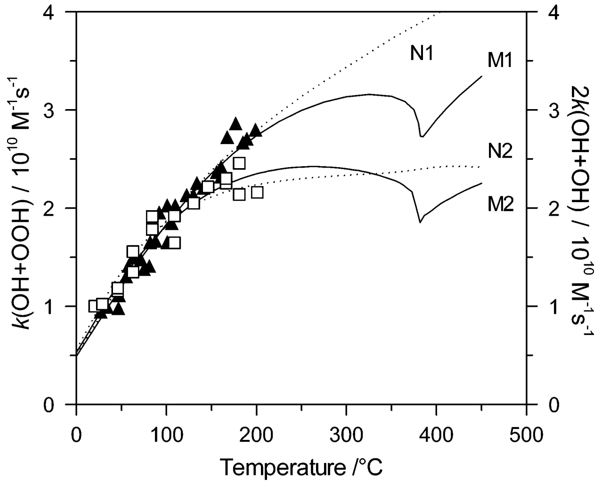

Figure 3. Temperature dependence of the rate constants for the self-termination reaction of the hydroxyl radical (triangles) and the reaction of the hydroxyl radical with OOH (squares) in water. The experimental data[8,17] are plotted on the same vertical scale, but $2k$ is used for the dimerization reaction. Lines N1 and N2 show the fits and extrapolations according to Elliot[9] ($A = 7.38 \times 10^{10}$ M^{-1} s^{-1}, $E_a = 3.0$ kJ mol^{-1} and $A = 2.18 \times 10^{10}$ M^{-1} s^{-1}, $E_a = -0.75$ kJ mol^{-1}), whereas examples of simulations using the multiple collisions model are denoted by curves M1 ($A = 1.0 \times 10^{11}$ M^{-1} s^{-1}, $E_a = 4.0$ kJ mol^{-1}, $p_R = 1.0$) and M2 ($A = 4.4 \times 10^{10}$ M^{-1} s^{-1}, $E_a = 1.5$ kJ mol^{-1}, $p_R = 1.0$).

predictions for the reaction between OH radicals and H atoms

$$H + OH \rightarrow H_2O \tag{8}$$

Clearly, the lines M1, M2, and M3 represent a whole family of parameter sets consistent with the experimental data. The point we wish to make is that they are just as valid as the model represented by line N and that extrapolations based on any one set of model parameters could easily result in a factor of 2 error for the rate constants under supercritical conditions.

The inadequacy of published data is further demonstrated in Figure 3, which compares results for two similar reactions

$$OH + OH \rightarrow H_2O_2 \tag{9}$$

$$OH + HO_2 \rightarrow O_2 + H_2O \tag{10}$$

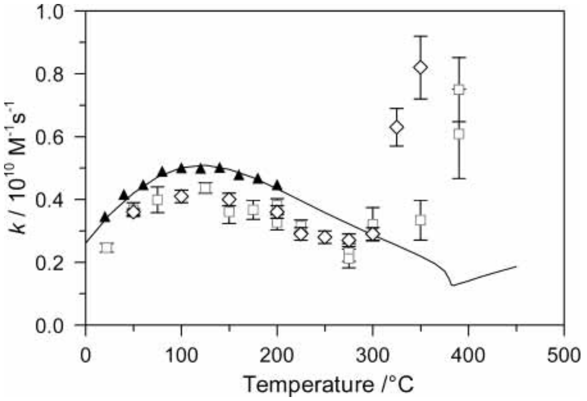

Figure 4. Temperature dependence of the rate constant for the reaction of the hydroxyl radical with nitrobenzene in water. The multiple collisions model (—) was adjusted to simulate the Leeds data[19] (triangles) using parameters $A = 2.2 \times 10^{10}$ M^{-1} s^{-1}, $E_a = 4$ kJ mol^{-1}, $p_R = 0.12$. It can also account for the Notre Dame[20] (squares) and Argonne[21] data (diamonds) up to 300 °C but not the rapid increase in the rate constant near the critical point.

The rate constant data[8,17] are plotted on a common scale to emphasize their similarity (as long as $2k$ is used for the dimerization reaction). It is evident that there is only significant difference in the region close to 200 °C and that these few data points dictate very different extrapolations, whether one follows the analysis of Elliot et al.[8,9] (lines N1 and N2) or our multiple collisions model (lines M1 and M2).

To distinguish between models and extract empirical parameters, it is necessary to have reliable kinetic data over a wide enough temperature range that any maximum or plateau is clearly defined. Unfortunately, this is not the case for the reactions involved in the radiolysis of water, with the exception of the self-reaction of hydrated electrons. The apparent negative activation energy for the latter reaction was rationalized by proposing the existence of an undetected intermediate, such as the dielectron.[18] On the other hand, Buxton et al.[11] demonstrated that the rate constants of many other reactions of the hydrated electron also go through a maximum as the temperature is raised. They interpreted this behavior in terms of reversible electron attachment

$$e_{aq}^{-} + X \rightleftharpoons X^{-} \rightarrow \text{products} \tag{11}$$

Similar kinetic behavior was later found for reactions of OH with aromatic compounds, and this was explained by transient formation of a π complex prior to either formation of the σ-bonded hydroxycyclohexadienyl radical product, or separation of the reactants[19]

$$OH + PhX \rightleftharpoons [HOPhX]_{\pi} \rightarrow HOPhX \tag{12}$$

This mechanism was also invoked to model more recent data, which extends into the supercritical region.[20] However, it is important to realize that the reaction models expressed by eqs 11 and 12 have the same general form as the multiple collisions model. Thus, reactants come together to form a transient intermediate or (in our model) an encounter pair, from which there is competition between forward reaction to form the product and a backward process leading to separation of the reactants. Figure 4 shows that our multiple collisions model can simulate the Leeds data[19] without invoking a π complex. On the other hand, our model fails to describe the rapid increase in the rate constant close to the critical point recently reported in independent work from Notre Dame[20] and Argonne.[21] The discrepancy between the high temperature rate constants derived from these two pulse radiolysis studies is attributed to complex kinetics involving multiple absorbing species, specifically the H and OH adducts of nitrobenzene.[21] This is particularly serious because the yield of H atoms has been found to increase dramatically in supercritical water.[22]

IV. Discussion and Conclusions

As kinetics measurements are extended to higher temperatures, more and more aqueous reactions are found to exhibit non-Arrhenius temperature dependence. Because such behavior is common to a wide range of reactants and reaction types, it is our belief that the key factor is the solvent-driven dynamics. Our multiple collisions model can account for existing kinetics data, but its predictions should be considered only indicative, not quantitative. Apart from the errors inherent in the approximate formulas used to estimate collision rates and encounter times, there are several effects which could lead to deviations at high temperatures. Thus, few of the model parameters can be expected to be constant as the water properties change. For example, A and E_a could both be affected if the degree or nature of reactant solvation changes with temperature and density. Also, setting $\beta = 1$ for radical−radical reactions involving OH is only justified if the electron spin−lattice relaxation time is less than the encounter duration.[16] This may be reasonable at room temperature, but it is unlikely at high temperature, where $\beta = 0.25$ should be used for a pair of spin doublet radicals, assuming there is no significant mixing of the radical pair singlet and triplet states.

It should be emphasized that these deficiencies are not unique to the multiple collisions model and are likewise ignored by the extrapolations commonly employed to model radiolysis of water in nuclear power reactors. In addition, modeling of reactor coolant chemistry[1−4,9] has not taken account of pressure effects. Clearly, it is imperative to extend measurements of rate constants to higher temperatures and to develop more sophisticated simulations of reactions in high-temperature water.

Acknowledgment. We thank Dr. David Bartels of Argonne National Laboratory for helpful comments and for sending copies of his work on pulse radiolysis of supercritical water prior to publication. This research was financially supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Model parameters and other data necessary to reproduce the simulations depicted in Figures 1−4. This material is available free of charge via the Internet at http://pubs.acs.org.

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