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A Kinetic Study of OH Radical Reactions with Methane and Perdeuterated Methane

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We measured absolute rate coefficients for the reactions of the hydroxyl radical with methane (k_1) and methane-d_4 (k_2) using the laser photolysis/laser-induced fluorescence technique. We characterized k_1 and k_2 over the temperature range 293–800 K at pressures between 400 and 750 Torr of helium. We find excellent agreement between our results and the recent determinations of k_1 at lower temperatures by Vaghjiani and Ravishankara. The measured rate coefficients, in the units cm^3 molecule^{-1} s^{-1}, fit well to the three-parameter expressions $k_1(T) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$ and $k_2(T) = 8.70 \times 10^{-22} T^{3.23} \exp(-1334/T)$. The kinetic isotope effect for abstraction of the H and D atoms varies from 6.75 at 293 K to 1.96 at 800 K. We compare our results to recently reported calculations by Melissas and Truhlar.

Introduction

Hydrogen atom abstraction from hydrocarbons by hydroxyl radical plays a key role in the chemistry of atmospheric and combustion processes. Numerical modeling of these phenomena requires a large database of accurate rate coefficients spanning a wide range of temperatures and pressures. Among the hydrocarbons, methane is the most prominent greenhouse gas with a steadily rising concentration in the atmosphere.[1] The primary depletion channel for atmospheric methane is reaction with OH, and accurate determination of this reaction rate coefficient is of obvious practical importance. This reaction is also one of the two major chain-propagation steps in the combustion of methane.[2] Kinetic measurements of this process at elevated temperatures are thereby of crucial significance.

Vaghjiani and Ravishankara[3] reported recently measurements of the rate coefficient, k_1, for the reaction

$$\mathrm{OH} + \mathrm{CH_4} \xrightarrow{k_1} \mathrm{H_2O} + \mathrm{CH_3} \qquad (1)$$

over the temperature and pressure ranges 223–420 K and 100–300 Torr (He or N_2). They derived the three-parameter expression $k_1(T) = 1.59 \times 10^{-20} T^{2.84} \exp(-978/T)$ cm^3 molecule^{-1} s^{-1} to represent their data. On average, Vaghjiani and Ravishankara's $k_1(T)$ measurements are ~25% smaller than previously accepted values, a significant deviation given the critical importance of reaction 1. As expected for a direct reaction, they found k_1 to be insensitive to total pressure. Prior to their study, numerous investigators measured $k_1(T)$ with varying techniques and conditions, and Atkinson[4] fit these results with the expression $k_1(T) = 6.95 \times 10^{-18} T^2 \exp(-1282/T)$ cm^3 molecule^{-1} s^{-1}. From this expression, one may derive $k_1(298\text{ K}) = 8.36 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, contrasted to Vaghjiani and Ravishankara's measurement of $k_1(298\text{ K}) = 6.25 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. As discussed by Vaghjiani and Ravishankara, this discrepancy is most likely due to impurity and secondary reactions of OH in the earlier studies.

In this letter, we report the results of our measurements of the rate coefficients for the reactions of OH with CH_4 (k_1) and CD_4 (k_2) over the temperature range 293–800 K at pressures of 400–750 Torr of helium. To our knowledge, this study is the first to examine the temperature dependence of k_2. Our experiments serve to confirm and extend the lower $k_1(T)$ determinations of Vaghjiani and Ravishankara and to provide precise data on the variation of the kinetic isotope effect, k_1/k_2, over a broad temperature range. These measurements provide a benchmark for comparison with theoretical predictions of rate coefficients and assist in the evaluation of models used to describe kinetic isotope effects, in particular, the treatment of tunneling. We compare our results with the recent calculations of Melissas and Truhlar,[5,6] who utilized *ab initio* methods and variational transition-state theory to compute $k_1(T)$ and $\{k_1/k_2\}(T)$.

Experimental Technique

We performed all experiments using the laser photolysis/laser-induced fluorescence technique described in detail in previous papers.[7,8] Briefly, OH formed upon 193-nm dissociation of H_2O, and we measured time-resolved [OH] profiles as a function of the CH_4 or CD_4 number density. A typical photolysis flux was ~5 mJ/cm^2. We excited the $R_1(3.5)$ line in the (0,0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ OH transition using an intracavity-doubled, CW, ring dye laser operating near 307 nm. We averaged the signal that results from 1000 to 5000 excimer-laser shots to produce each [OH] profile.

We conducted all experiments under slow-flow conditions, such that each photolysis pulse initiated reaction within a locally fresh gas sample. A mixture of methane/helium, H_2O/helium, and helium diluent conditioned the reactor prior to the onset of data collection, thereby minimizing any effects due to methane adsorption on the reactor walls. The gas temperature in the reaction zone, measured with a retractable chromel/alumel thermocouple, was constant to ±3 K over both the dimensions of the probed volume and the duration of the experiment.

All reactions proceeded under pseudo-first-order kinetic conditions with [OH] ≪ [methane]. Typical initial OH concentrations were ~1×10^{11} molecules cm^{-3}, several orders of magnitude smaller than the lowest methane concentrations utilized. At lower temperatures, where k_1 and k_2 are small, we used very large methane concentrations, e.g., $[CD_4] = 5 \times 10^{17}$ molecules cm^{-3} at 293.5 K, to negate the importance of OH reactions with product methyl radicals. Because methane is an efficient quencher of OH fluorescence, we averaged many excimer-laser shots in these low-temperature experiments. We extract diffusion-corrected decay constants $k' = k_i$[methane] from the [OH] profiles and then determine bimolecular rate coefficients, $k_i(T)$, from the slope of the least-squares straight line through the ([methane], k') data points.

The chemicals utilized in this study had the following stated minimum purities: CH_4, 99.97%; CD_4, 99.98% and 99.2% D-enriched; He, 99.9999%; and H_2O, HPLC organic-free reagent grade. GC analysis of the methane samples detected only trace

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TABLE I: Rate Coefficient and Kinetic Isotope Effect Data for the Reaction of OH with Methane

	$10^{15}\,k$,[a] cm^3 molecule^{-1} s^{-1}		
temp (K)	k_1	k_2	$\{k_1/k_2\}$[a]
293	5.62 ± 0.43	0.83 ± 0.08	6.75 ± 0.83
333		2.15 ± 0.18	5.74 ± 0.48[b]
365		4.22 ± 0.32	4.94 ± 0.37[b]
409	37.1 ± 2.2	9.10 ± 0.58	4.04 ± 0.35
420	42.2 ± 2.3		
459		19.1 ± 1.1	
498	101 ± 4	30.6 ± 2.2	3.30 ± 0.27
547	152 ± 10	53.0 ± 3.2	2.87 ± 0.26
602	237 ± 14	90.0 ± 5.6	2.63 ± 0.22
654	367 ± 22	150 ± 10	2.45 ± 0.22
704	474 ± 26	197 ± 12	2.31 ± 0.19
745	576 ± 32		
753		302 ± 18	1.99 ± 0.12[b]
800	756 ± 42	385 ± 24	1.96 ± 0.16

[a] Error specifications represent ±2σ estimates of the total experimental uncertainty. [b] For these points, we compute k_1 from the expression $k_1(T) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1}.

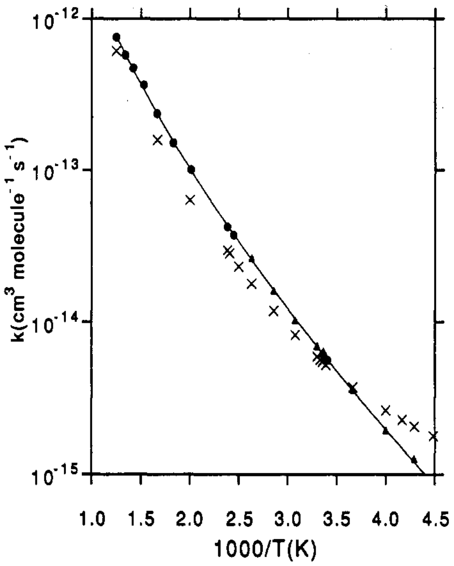

Figure 1. Arrhenius plot of the rate coefficients for the reaction of OH with CH_4: ●, this work; ▲, ref 3; ×, CVT/SCT calculations, ref 5. The solid line represents the best fit to the combined (●) and (▲) data sets, $k_1(T) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1}. The estimated experimental errors are comparable to the size of data symbols.

impurities (<0.01%) of ethanes, levels that are too small to contribute significantly to the observed [OH] decay rates.

Results and Discussion

Table I lists the bimolecular rate coefficients determined in this study for the reactions $OH + CH_4 \rightarrow H_2O + CH_3(k_1)$ and $OH + CD_4 \rightarrow HDO + CD_3(k_2)$. Figure 1 displays an Arrhenius plot of our $k_1(T)$ data along with those from selected previous studies. The agreement between our measurements and those of Vaghjiani and Ravishankara is outstanding, and we confirm and extend (in T) their smaller $k_1(T)$ values. A least-squares fit of both data sets yields the recommended expression for $223 \le T \le 800$ K, $k_1(T) = 9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$ cm^3 molecule^{-1} s^{-1}.

Recently, Melissas and Truhlar[5] computed $k_1(T)$ by applying interpolated variational transition-state theory and a multidimensional tunneling correction (CVT/SCT) to a potential energy surface calculated with *ab initio* methods. As shown in Figure 1, their $k_1(T)$ values, while generally in good agreement with the measurements, display more curvature at all temperatures than do the experimental determinations.

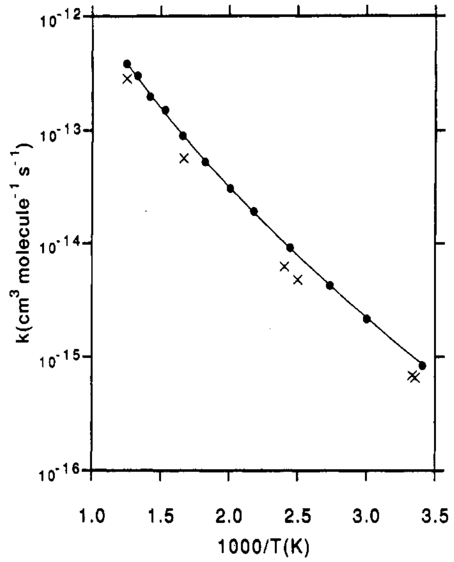

Figure 2. Arrhenius plot of the rate coefficients for the reaction of OH with CD_4: ●, this work; ×, CVT/SCT calculations, refs 5 and 6. The solid line represents the best fit to our (●) data, $k_2(T) = 8.70 \times 10^{-22} T^{3.23} \exp(-1334/T)$ cm^3 molecule^{-1} s^{-1}. The estimated experimental errors are comparable to the size of data symbols.

Figure 2 displays an Arrhenius plot for the reaction $OH + CD_4 \rightarrow HDO + CD_3(k_2)$. The solid line depicts our recommended best fit, $293 \le T \le 800$ K, $k_2(T) = 8.70 \times 10^{-22} T^{3.23} \exp(-1334/T)$ cm^3 molecule^{-1} s^{-1}. The only prior experimental determination of k_2 is that by Gordon and Mulac,[9] $k_2(416\text{ K}) = (5.0 \pm 0.17) \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. This rate coefficient is a factor of 2 smaller than that computed from our best-fit expression. While we cannot specify the origin of this discrepancy, we believe that reactive interferences are more likely to occur in the less controllable pulse radiolysis environment utilized by Gordon and Mulac than in our experimental configuration. Figure 2 also displays $k_2(T)$ values computed from Melissas and Truhlar's CVT/SCT calculations on $k_1(T)$ and $\{k_1/k_2\}(T)$. These data are in fair agreement with our results over the temperature range 293–800 K, displaying qualitatively the same deviations as seen for the reaction $OH + CH_4 \rightarrow H_2O + CH_3(k_1)$.

In our studies of k_1 and, particularly, k_2, the most obvious potential interference in our determinations was reaction of OH with product methyl radicals. Since OH reacts with CH_3 about 15 000 times faster than it does with CH_4 at room temperature,[10] it is crucial to maximize the ratio [methane]/$[OH]_0$ at reaction inception. For our room-temperature experiments on k_2, we utilized $[CD_4]$ levels that were of order 5×10^6 larger than $[OH]_0$. If OH reacts with CD_3 at the same rate as with CH_3, then ~2% of the OH decay rate could be attributed to this secondary process. For these conditions, a 50% decrease in 193-nm photolysis flux (and thus $[OH]_0$) had no effect on the measured k_1 and k_2 values. Thus, we believe our measurements to be largely free of kinetic interferences.

Figure 3 displays the deuterium kinetic isotope effect, $\{k_1/k_2\}(T)$, measured in this work and computed by Melissas and Truhlar.[6] We find that our data fits well to the expression $\{k_1/k_2\}(T) = (0.95 \pm 0.03) \exp[(598 \pm 24)/T]$ for $293 \le T \le 800$ K. While differences do exist between our measurements and the CVT/SCT results of Melissas and Truhlar, the overall level of agreement is excellent, as the deviations between experiment and theory for k_1 and k_2 largely cancel. At $T = 416$ K, for example, our best-fit expression yields $k_1/k_2 = 4.00$ and Melissas and Truhlar compute $k_1/k_2 = 4.53$, whereas Gordon and Mulac report $k_1/k_2 = 11$. This latter discrepancy is enormous, and it suggests that the pulse radiolysis experiments may be in error.

In this Letter, we describe precise measurements of the rate coefficients for the reactions $OH + CH_4 \rightarrow H_2O + CH_3(k_1)$ and

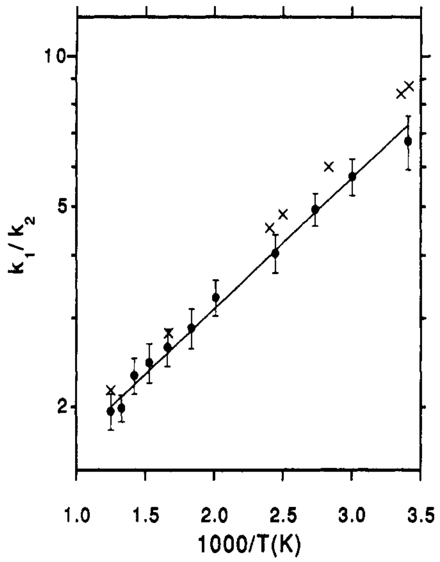

Figure 3. Kinetic isotope effect, $\{k_1/k_2\}$, plotted as a function of $1000/T$ (K): ●, this work; ×, CVT/SCT calculations, refs 5 and 6. The solid line displays the best fit to our data, $\{k_1/k_2\}(T) = 0.95 \exp(598/T)$. Error bars represent $\pm 2\sigma$ estimates of the total experimental uncertainty.

$OH + CD_4 \rightarrow HDO + CD_3 (k_2)$. We confirm and extend (in T) the smaller k_1 values of Vaghjiani and Ravishankara, and we obtain excellent agreement with the CVT/SCT calculations of Melissas and Truhlar on the kinetic isotope effect $\{k_1/k_2\}(T)$. Our data provide an experimental benchmark for comparison with rate parameters calculated theoretically.

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