THE REACTION OF OH AND OD WITH NITROMETHANE AND OD WITH PERDEUTERONITROMETHANE

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Laser photolysis/laser-induced fluorescence (LIF) is employed to investigate the kinetics of the reactions, $OH + CH_3NO_2$, $OD + CH_3NO_2$, and $OD + CD_3NO_2$ over the temperature range 296-671 K. Photolysis of nitromethane at 266 nm generates OH or OD radicals. Rate constants are independent of pressure over the range 100-300 Torr. The following Arrhenius equations are calculated: $k = (1.1 \pm 0.4) \times 10^{-12} \exp[-(2730 \pm 290 \text{ cal/mol})/RT]$ cm³ s⁻¹ for OH, $OD + CH_3NO_2$ and $k = (5.3 \pm 2.4) \times 10^{-13} \exp[-(2860 \pm 340 \text{ cal/mol})/RT]$ cm³ s⁻¹ for OD + CD₃NO₂. A hydrogen atom abstraction mechanism is supported by evidence from isotopic studies, transition-state theory calculations, absence of pressure effects, known energetics, and measured activation energies. Transition-state theory (TST) calculations predict non-Arrhenius behavior as temperatures approach the combustion regime. The TST calculation is fit by the equation, $k = 4.37 \times 10^{-20} T^{2.4} \exp(-340/T)$ cm³ s⁻¹, over the temperature range 200-2000 K.

1. Introduction

The hydroxyl radical, OH, is an important intermediate in combustion, detonation, photochemical smog, and flames [1,2]. However, its role in these processes has not been quantitatively characterized. Rate coefficients have been determined for the reaction of OH with many organic compounds [3] but studies involving the reaction of OH with organic compounds that contain NO₂ groups are scarce [4-8]. Organic compounds that contain NO₂ groups are important as energetic materials and have been observed as trace atmospheric constituents. The OH radical may be a very important intermediate or chain carrier in the detonation of energetic materials containing C, H, N, O constituents. Also, reactions with OH are known to be one of the most important removal pathways for trace organic compounds in the atmosphere.

Nitromethane, CH_3NO_2 , is relevant as a model compound for energetic materials and as a model of nitro-compounds that may be present in the

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troposphere in regions of photochemical smog. The only rate constant reported for OH + nitromethane is that of Campbell and Goodman [4] performed at room temperature by an indirect, relative-rate technique.

Here we report the first direct measurements for the rate coefficients of OH with nitromethane. Laser photolysis of nitromethane is employed for production of OH and laser-induced fluorescence (LIF) is used to monitor the relative OH radical concentration. Additional experiments with perdeuterated nitromethane, CD_3NO_2 , allows study of the reactions $OD + CH_3NO_2$ and $OD + CD_3NO_2$. The experimental results, along with TST calculations, are employed to deduce a reaction mechanism for these reactions.

2. Experimental

The experimental apparatus was similar to other radical-molecule studies performed in this laboratory [9-13]. OH (OD) radicals were produced by photodissociation of nitromethane (or perdeuteronitromethane) by the fourth harmonic of a

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Nd³⁺: YAG laser (Quanta-Ray DCR1A) at 266 nm. The photolysis laser was typically operated at energies of 1–3 mJ/pulse at a repetition rate of 10 Hz. At an adjustable time delay after the photolysis pulse (jitter < 1 µs), a dye laser (Lambda Physik FL-2002) pumped at 532 nm by a doubled Nd³⁺: YAG laser (Quanta-Ray DCR-1A) operating at 10 Hz, was frequency doubled ($\approx 100 \mu$ J/pulse) and used to excite LIF from the OH radicals on the Q₁(2) rotational line at 307.99 nm of the (A²Σ⁺-X²Π_i), (0, 0) vibronic band. For the OD experiments, the Q₁(3) transition at 307.4 nm was utilized. The dye and photolysis laser beams were collinearly counterpropagated through the reaction cell.

Fluorescence from the reaction zone was collected at right angles to the laser beams with quartz lenses and appropriate filters designed to pass the region around 308 nm. An RCA 31000B photomultiplier tube was used to detect the fluorescence. The output of the photomultiplier was sent to a boxcar averager/gated integrator (SRS-250) operating as a gated integrator. The output of the boxcar was digitized and stored by a laboratory microcomputer (DEC MNC11/23). Facilities were also available to monitor the power output of the dye and photolysis lasers by the boxcar/ computer system. The computer controlled the delay between the lasers, stored the data, and was also utilized for data analysis. Typical kinetic runs spanned time delays from -10 to 6000 μ s.

The reaction cell, a resistively heated pyrex cross, has been previously described [14]. A thermocouple positioned about 5 mm above the laser beams measured the temperature in the cell. All experiments were conducted on slowly flowing $(\sim 0.5 \ \ell/\min)$ gas mixtures in order to minimize interference by photolysis and reaction products. All reactants were diluted in argon and stored in 20 ℓ glass reservoirs. Pressures were measured by a capacitance manometer (MKS). The concentration of each gas was computed from the partial pressure of its mixture used in the flow. Experiments were performed at 100 Torr total pressure using argon as the buffer gas except for a series of experiments performed at 300 Torr of argon to test the pressure effect on the reactions.

CH₃NO₂ was obtained from Eastman and dis-

tilled on an auto annular spinning band column. Only samples that exhibited no extraneous gas chromatographic peaks were employed. CD_3NO_2 (99%, Wilmad Glass Co.) was distilled trap-to-trap before use.

3. Results

The LIF intensity was taken as a relative measure of the OH(X² Π_i) concentration. The LIF signal decayed exponentially as a function of delay time, *t*, after the photolysis pulse. The data were fit by a nonlinear least-squares computer program to the function

$$I = A \exp(-k_1 t) + B,$$

where I is the LIF signal intensity and k_1 is the pseudo-first-order decay rate constant for OH due to all loss processes, i.e. reaction and diffusion out of the beam. The OH decay rate should be proportional to the concentration of added reactant gas. Second-order rate constants, k_2 , for OH + reactant were obtained by linear least-squares fits to the equation

$$k_1 = k_0 + k_2$$
[reactant],

where k_0 is the loss rate for OH due to all other removal mechanisms including diffusion out of the laser beam. As a test of the experimental apparatus, the rate constant for OH + C₂H₆ was measured as a function of temperature. The photolysis of H₂O₂ was utilized for OH production. Our measured rate constants over the temperature range studied were within 10% of accepted literature values [15].

Initially, H_2O_2 was employed as the OH precursor in our attempts to measure the rate for this reaction. We have reported [16] an approximate upper limit for this reaction based on using both H_2O_2 and O_3 - H_2O systems as OH precursors. We have also reported that OH is produced in the photolysis of nitromethane at 266 nm [16,17]. Here we utilize the photolysis of CH₃NO₂ for production of OH radicals; therefore, CH₃NO₂ is both an OH precursor and a reactant in this study. We have demonstrated that OH is a prompt, single-



Fig. 1. Semi-log plots of LIF intensity minus background versus delay time for $OH + CH_3NO_2$ at 671 K and 100 Torr total pressure; $\bigcirc 0.35$ Torr CH_3NO_2 , $\Box 2.81$ Torr CH_3NO_2 .

photon product from the photodissociation of nitromethane at 266 nm with a quantum yield of 0.004 [17]. In the present experiments we observe that the OH concentration does not reach a maximum immediately upon photolysis. Actually, the $OH(X^2\Pi_i)$ concentration reaches a maximum in an amount of time that is related to the nitromethane concentration. The time of maximum OH concentration decreases as the nitromethane concentration increases. Thus, there seem to be two pathways for OH production - one, a prompt photodissociation process and the second as a result of reaction or collisional deactivation. In these kinetic experiments the OH decays were always measured after the initial rise in [OH] was complete which takes only a few microseconds.

Typical decays of the logarithm of the LIF signal intensity versus time are shown in fig. 1. Single-exponential decays were obtained under all conditions. Plots of pseudo-first-order decay rate constants at two temperatures are shown in fig. 2. These plots are from data taken at two different photolysis laser energies. Since we are employing nitromethane as the hydroxyl radical precursor, rate constants need to be obtained over a range of photolysis laser energies to check for effects due to



Fig. 2. Plots of k_1 versus CH₃NO₂ concentration for OH+ CH₃NO₂; \bigcirc 671 K and 3.0 mJ/pulse photolysis laser energy, \square 300 K and 1.9 mJ/pulse.

photolysis. Fig. 3 is a plot of measured rate constant versus photolysis laser energy at 100 Torr and 300 K. The photolysis laser energy was varied from 0.8 to 3.1 mJ/pulse. The figure demonstrates that there is an increase in the measured rates at greater laser energies. As the laser energy is increased by a factor of three, the measured rate constant increases by roughly a factor of three at this temperature. It is apparent that the photolysis of nitromethane is creating a species that is adding to the removal of OH radicals. These side reac-



Fig. 3. Plots of measured rate constant versus photolysis laser energy at 300 K and 100 Torr. Intercept yields the rate constant, $k = (1.41 \pm 0.30) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

tions become significant in the present system because of the relatively slow rate.

We have calculated the concentration of NO_2 and CH_3 radicals that are produced from photolysis at 266 nm.

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2$$
,

by use of the laser beam dimensions and energy along with the known extinction coefficient of nitromethane [18] and assuming a quantum yield of unity for the above process. At 3 mJ/pulse, 7×10^{13} cm⁻³ of both NO₂ and CH₃ are produced. Using rate constants of 4.1×10^{-12} cm³ s⁻¹ for the reaction OH + NO₂ \rightarrow HNO₃ (from DeMore et al. [19] at 100 Torr) and 9.0×10^{-11} for the reaction OH + CH₃ \rightarrow CH₃OH (from Tsang and Hampson [20]), results in pseudo-firstorder decay rates that can readily account for the increased rates observed here at larger photolysis energies.

In order to account for this photolysis effect at each temperature, rate constants were measured as a function of photolysis laser energy. The data obtained at each temperature were then plotted as in fig. 3 and least-squares fit by a straight line. The intercept of the plot yields the rate constant extrapolated to zero laser power. In this way we have corrected for the photolysis effect. Rate constants were obtained over the temperature range 299-671 K. Also, rate constants were obtained at room temperature for 100 and 300 Torr total pressure (mostly argon). The rate constants are tabulated in table 1. The results show that at room temperature there is no pressure effect on the measured rate coefficient. An Arrhenius plot of $\log k$ versus 1/T is shown in fig. 4.

In order to learn more about the mechanism of this reaction we have performed additional studies with perdeuteronitromethane, CD_3NO_2 . In these experiments, LIF was excited on the $Q_1(3)$ transition of OD near 307.4 nm. CD_3NO_2 was photolyzed, as in the non-deuterated case, to yield rate constants for the reaction, $OD + CD_3NO_2 \rightarrow$ products. The reaction $OD + CH_3NO_2$ was also studied. A small constant pressure (~400 mTorr) of CD_3NO_2 was flowed through the cell for the generation of OD radicals. Then the CH_3NO_2

Rate constant a) Reaction Temperature $(10^{-14} \,\mathrm{cm}^3 \,\mathrm{s}^{-1})$ (K) $OH + CH_3NO_2$ 299 ^{b)} 1.74 ± 0.38 300 1.41 ± 0.30 372 2.73 ± 0.85 473 5.80 ± 1.40 572 7.35 ± 0.71 19.3 ± 3.0 671 $OD + CH_3NO_2$ 296 0.82 ± 0.44 378 1.86 ± 0.82 474 4.43 ± 0.04 572 8.48 ± 1.22 671 21.8 ± 1.0 296 ^{b)} $OD + CD_3NO_2$ 0.50 ± 0.02 299 0.49 ± 0.06 376 0.74 ± 0.13 475 2.33 ± 0.08 566 3.82 ± 0.13

a) All measurements performed at 100 Torr total pressure (mostly argon) unless otherwise indicated. Listed uncertainties are 1σ and result from least-squares fit only. Estimated overall uncertainty is ±50%.

 8.46 ± 0.06

670

^{b)} 300 Torr total pressure.



Fig. 4. Arrhenius plots for OH(OD) + nitromethane reactions;
 OH + CH₃NO₂, □ OD + CH₃NO₂, △ OD + CD₃NO₂. Top line is the fit to the OH and OD + CH₃NO₂ data, bottom line is the fit to the OD + CD₃NO₂ data.

Table 1						
Measured	rate	constants	for	the	reactions	$OH + CH_3NO_2$,
$OD + CH_2$	NO ₂	and OD +	- CD	NC)_	

concentration was varied to generate second-order plots. Also attempted was the study of the OH + CD_3NO_2 reaction. Unfortunately, the small pressure of CH_3NO_2 required for the generation of OH radicals resulted in pseudo-first-order decays that prevented the slower OH + CD_3NO_2 from being measured reliably.

The data for these three reactions, extrapolated to zero photolysis laser energy, are listed in table 1. All uncertainties are 1σ and represent statistical precision of the least-squares fits only. These reactions have been studied over the temperature range 296–671 K. Both OD + CD₃NO₂ and OH + CH₃NO₂ have been studied at 100 and 300 Torr. Within experimental error no pressure effects are apparent. The data for all the reactions are plotted in Arrhenius form in fig. 4. The results of leastsquares to the Arrhenius equation are:

$$k = (8.1 \pm 3.2) \times 10^{-13}$$

$$\times \exp[-(2400 \pm 300 \text{ cal/mol})/RT] \text{ cm}^3 \text{ s}^{-1};$$

$$OD + CH_3NO_2,$$

$$k = (1.8 \pm 1.0) \times 10^{-12}$$

$$\times \exp[-(3300 \pm 400 \text{ cal/mol})/RT] \text{ cm}^3 \text{ s}^{-1};$$

$$OD + CD_3NO_2,$$

$$k = (5.3 \pm 2.4) \times 10^{-13}$$

$$\times \exp[-(2860 \pm 340 \text{ cal/mol})/RT] \text{ cm}^3 \text{ s}^{-1}.$$

We have also fit the combined data for OD and OH reacting with CH_3NO_2 , this yields:

OH/OD + CH₃NO₂,

$$k = (1.1 \pm 0.4) \times 10^{-12}$$

 $\times \exp[-(2730 + 290 \text{ cal/mol})/RT] \text{ cm}^3 \text{ s}^{-1}.$

4. Discussion

 $OH \perp CH NO$

The present results are the only directly measured rate constants for the hydroxyl-nitromethane reaction. Two possible reaction channels and their energetics are shown below, hydrogen atom abstraction or OH addition to the nitrogen atom followed by subsequent scission of the C-N bond, i.e.

$$OH + CH_3NO_2 \rightarrow H_2O + CH_2NO_2,$$

$$\Delta H = -17.8 \text{ kcal/mol}, \qquad (1)$$

$$OH + CH_3NO_2 \rightarrow CH_3NO_2 \rightarrow CH_3 + HNO_3,$$

$$OH$$

$$\Delta H = 10.7 \text{ kcal/mol}. \qquad (2)$$

 ΔH for reaction (2) is calculated from the compiled data of Benson [21]. ΔH for reaction (1) is calculated from the heats of formation of Melius [22]. It is apparent that the addition reaction is not energetically favorable. The fact that the room temperature rate constant does not vary with pressure between 100 and 300 Torr argon is also evidence against reaction (2). The presently reported activation energy, $E_a = 2.7$ kcal/mol, is similar to other H-atom abstraction reactions by OH [3]. As discussed below, a transition-state-theory model for the H-abstraction process is successful in reproducing the temperature dependence of the data. The only previous literature value for the OH-nitromethane reaction is the relative-rate work of Campbell and Goodman [4]. They reported a rate constant of $(9.2 \pm 1.0) \times$ 10^{-13} cm³ s⁻¹ at 292 K. We are not able to reconcile the factor of about 60 difference in their value with our much slower room temperature rate coefficient. Our value is in line with the recent work of Gaffney et al. [8] on the direct measurement of the absolute rate constant for a similar reaction, OH + CH₃ONO₂, $k = (3.4 \pm 0.4) \times$ 10^{-14} cm³ s⁻¹ at 298 K. Recently, Kerr and Stocker [23] have reported a relative-rate measurement on the OH + CH₃ONO₂ reaction of k = (3.7) ± 0.9) $\times 10^{-13}$ at 303 K. Thus there appears to be a major inconsistency (one order of magnitude) between the direct measurements and relative-rate techniques in the reported rate constants for these $OH + NO_2$ -containing hydrocarbon reactions. There is a similar controversy in the measurements of rate constants for the OH + CH₃ONO reaction [3,24-26].

The Arrhenius plot of fig. 4 demonstrates that within experimental uncertainty the measured rate

constants for the two reactions, $OH + CH_3NO_2$ and $OD + CH_3NO_2$, are identical. This result is expected for an abstraction of this type; the hydrogen atom on the abstracting hydroxyl radical is not involved in bond forming or breaking and therefore the effect of this isotopic substitution (i.e. the secondary isotope effect) will be negligible. This is discussed in further detail below with reference to the transition-state theory calculation. In contrast, the rate constants for the OD + CD₃NO₂ reaction are a factor of two lower than the CH₃NO₂ reactions due to the primary kinetic isotope effect [27]. A simple harmonic oscillator treatment predicts that for a C-H vibrational frequency of 3000 cm^{-1} , the rate constant for the deuterated reaction will be lower by a factor of two at 700 K and a factor of five at 300 K [28]. In the present data, the rate constant for the CD_3NO_2 reaction is a factor of two lower across the entire temperature range. The simple harmonic oscillator treatment predicts that the activation energy of the reactions should differ by 1.2 kcal/mol in contrast to the present result of very similar activation energies. These differences from theoretical expectations must be considered in light of the experimental uncertainty of the present measurements. As the rate constants result from extrapolations to zero laser power they are much more uncertain than most rates determined by this experimental technique. Overall uncertainties of $\pm 50\%$ are estimated. Thus the disagreement with theory could be due to this uncertainty.

Transition-state theory was incorporated to model the $OH + CH_3NO_2$ abstraction reaction to test the plausibility of the proposed reaction mechanism and also to attempt to extrapolate the data into the combustion temperature regime. The transition state configuration involves hydrogen atom abstraction by the OH radical from nitromethane. The geometry assumes, for simplicity, collinear H-O and C-H bonds and a HO-H bond distance of 1.5 Å. Other similar transitionstate geometries appropriate for H abstraction give approximately the same results. The moments of inertia and frequencies for the reactants and the transition state are listed in table 2. The geometry and frequencies for nitromethane are from the work of Trinquecoste et al. [29].

 Table 2

 Parameters used in the transition-state theory calculation

	OH	CH ₃ NO ₂	Transition state
moments of inertia (amu Å ²)	0.888	45.19, 42.11, 84.18	44.68, 201.3, 242.9
vibrational frequencies (cm ⁻¹)	3735	480, 607, 657, 918, 1104, 1378, 1402, 2968, 3065, 1426, 1103, 1426, 1561, 3045 ^{a)}	480, 607, 657, 918, 1104, 1378,1402, 2968, 3065, 1426, 1103, 1426, 1561, 3045, 3735, 307(4) ^{b)}

^{a)} Both CH₃NO₂ and the transition state have an internal rotation that has not been included due to the fact that its moment of inertia will cancel out in the calculation.

^{b)} The number in parentheses indicates the degeneracy of the listed frequency.

The new frequencies of the transition state are assumed, for simplicity, to be degenerate. The computer program incorporates a nonlinear leastsquares routine in which both the barrier height at 0 K, E_0 , and the new, degenerate frequencies in the transition state are varied iteratively to give the best fit. The fit is shown in fig. 5. The fitting yields a value of $E_0 = 2.1 \pm 0.2$ kcal/mol. The result of the transition state calculation was fit by the functional form $k = AT^B \exp(-C/T)$ which



Fig. 5. Arrhenius plot of OH and $OD + CH_3NO_2$ data with the curve demonstrating the TST calculation result; \bigcirc OH+ CH₃NO₂, \Box OD + CH₃NO₂.

yields $k = 4.37 \times 10^{-20} T^{2.4} \exp(-340/T) \text{ cm}^3$ s^{-1} over the temperature range 200–2000 K. A similar calculation was performed for the two deuterated reactions. As expected, the presence of deuterium in the $OD + CH_3NO_2$ reaction had no effect on the calculation. This small change in mass only had a very small effect on the moments of inertia of the species involved. The calculation performed for the $OD + CD_3NO_2$ reaction also gave very similar results. The frequencies and E_0 required to fit the data were almost identical to those in the first calculation. Fig. 5 demonstrates that the TST calculation predicts an upward curvature of the Arrhenius plot with increasing temperature. This is a common result of these calculations which results from the low vibrational frequencies in the transition state that are required to match the measured rate constants.

5. Conclusions

Absolute rate constants for the $OH + CH_3NO_2$ reaction have been measured over the temperature range 299–671 K. Additionally, studies were also performed on the reaction $OD + CH_3NO_2$ and $OD + CD_3NO_2$. A mechanism involving hydrogen atom abstraction is supported by isotopic studies, transition-state theory calculations, absence of pressure effects, known energetics, and measured activation energies. TST calculations predict non-Arrhenius behavior as temperatures approach the combustion regime.

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