



Lifetime of the CH3OH* intermediate in the reaction CH4+O(1 D 2) \rightarrow CH3OH* \rightarrow CH3+OH

Roger D. van Zee and John C. Stephenson

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COMMUNICATIONS

Lifetime of the CH₃OH* intermediate in the reaction $CH_4 + O(^1D_2) \rightarrow CH_3OH^* \rightarrow CH_3 + OH$

Roger D. van Zee and John C. Stephenson

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Subpicosecond lasers measured the appearance rate of OH X(v=0) following 267 nm photolysis of the $CH_4 \cdot O_3$ van der Waals complex. The rise of the OH A \leftarrow OH X laser-induced fluorescence with respect to the photolysis/probe delay time, t_D , was $\text{LIF}(t_D) = 1 - \exp(-t_D/\tau)$ with τ approximately 3 ps, indicating that the reaction $CH_4 + O(^1D_2) \rightarrow CH_3 + OH$ involves a CH_3OH^* intermediate with that lifetime. No prompt OH(v=0) from a direct or fast reaction was observed. © 1995 American Institute of Physics.

Because of its importance in combustion and atmospheric chemistry, the reaction between CH_4 and $O({}^1D_2)$ has been the subject of numerous investigations, including chemical quenching¹⁻³ and molecular beam⁴ experiments, spectroscopic measurements of the energy content of the $H^{5,6}_{2,6}$ OH,⁷⁻¹⁴ and CH₃ ^{15,16} products, and *ab initio* studies.¹⁷ The chemical and beam results show that the formation of CH_3+OH (~75%) and CH_3O+H (~25%) dominate. Very small yields, if any, are found in CH₂O+H₂, CH₂+H₂O, and $CO+2H_2$. Despite this large body of work, the nature of the transition state for the dominant channel, $CH_4 + O({}^1D_2)$ \rightarrow CH₃(v,J)+OH(v,J) [Δ H(0 K)=-182.0 kJ mol⁻¹] remains controversial. It has been hypothesized¹⁻¹⁷ that some OH is formed from an excited methanol (CH₃OH^{*}) transition state, in which energy is randomized among the vibrations before fragmentation into CH₃ and OH, with a unimolecular decay rate consistent with statistical theories. Other OH may be formed from a very short-lived transition state from either an H-stripping type trajectory or an insertion complex that decays before energy randomization. Evidence for a long-lived CH₃OH* transition state comes from chemical quenching studies^{1,2} of the $CH_4 + O(^1D_2)$ reaction, in which the quantum yield of CH₃OH increased with pressure as the CH₃OH* was collisionally stabilized before dissociation. Prompt OH production via a different mechanism was also suggested because significant OH was formed even at pressures where all CH₃OH* should have been stabilized. On the other hand, sub-Doppler spectroscopy¹⁰ showed that OH(v=4, N=8) formed in the reaction was scattered nearly isotropically in the center of mass, which is consistent with a transition state with a lifetime of at least one rotational period.

To obtain more direct evidence about the lifetime of the transition state involved in this reaction, we performed pump/probe experiments using subpicosecond lasers. The reaction was initiated when a pump laser photolyzed ozone in the precursor $CH_4 \cdot O_3$ van der Waals complex¹⁴ to form $O({}^{1}D_{2})$. The formation rate of OH(v,J) from the ensuing reaction between the oxygen atom and the adjacent methane molecule, $CH_4 \cdot O_3 + h\nu_{267 nm} \rightarrow CH_4 \cdot O(^1D_2) \cdot O_2 \rightarrow CH_3OH^*$ $+O_2 \rightarrow CH_3 + OH + O_2$, was determined by laser-induced fluorescence (LIF) spectroscopy of OH using a time-delayed probe pulse. This approach was first used¹⁸⁻²⁰ to determine the lifetime of the HOCO* intermediate in the reaction $CO_2 \cdot HI + h \nu_{uv} \rightarrow HOCO^* + I \rightarrow OH + CO + I$ and has also been applied to other reactions.²¹

Our laser apparatus consisted of a passively modelocked titanium doped sapphire (Ti:S) laser, which produced 90 fs pulses, approximately transform limited in spectral content and centered at 800 nm, at 100 MHz repetition rate. These pulses were stretched to 200 ps, amplified to 2 mJ at 20 Hz repetition rate in a home-built Ti:S regenerative amplifier, amplified to 20 mJ in a second Ti:S rod, and compressed to 110 fs. Part of this light was frequency tripled to give 200 μ J pulses at 267 nm for the photolysis laser. Part of the compressed 800 nm light generated a white light continuum, which was passed through a notch filter to select light near 500 nm. This 500 nm seed pulse was amplified in a series of dye cuvettes and summed with 800 nm to give 20 μ J pulses near 308.0 nm ($\Delta\lambda_{FHWM}$ ~2.5 nm) to probe the OH $A(^{2}\Sigma, v=0) \leftarrow OH X(^{2}\Pi, v=0)$ transitions. The crosscorrelation between the photolysis and probe was measured as the difference frequency (~2.0 μ m) in a 0.5 mm KDP crystal and found to have a Gaussian full-width at half maximum of 0.5 ps. The full energy of the laser beams was not used in order to avoid multiphoton processes and to ensure that the LIF signal was linear in photolysis and probe pulse energy. The supersonic expansion in which the van der Waals complexes were formed and the LIF detection apparatus were the same as in our earlier experiments,¹⁴ in which the distribution of rovibrational energy in the nascent OH was measured using high resolution, 10 ns pulse duration lasers. Also discussed in Ref. 14 is the evidence that the OH is formed in $CH_4 \cdot O_3$ clusters rather than larger clusters.

Figure 1 shows the OH LIF signal as a function of photolysis/probe delay time, t_D . In the upper trace, the probe laser at 308.0 nm excited predominantly the OH(v=0, low-J) lines; in the lower trace, the probe laser at 306.1 nmprobed predominantly OH(v=0, high-J) states.²² In both cases the signal increases as $LIF(t_D) = 1 - exp(-t_D/\tau)$. A



FIG. 1. Laser-induced fluorescence signal from OH(v=0) as a function of photolysis/probe time delay for CH₄·O₃+ $hv_{267 \text{ nm}}$ →CH₃+OH+O₂. For the lower trace, the probe wavelength was 306.1 nm, probing mostly OH X(v=0, high-J) states. For the upper trace the probe wavelength was 308.0 nm, probing mostly low-J states.²² The smooth curves through the data are fits to the functional form, $\text{LIF}(t_D)=1-\exp(-t_D/\tau)$ for $\tau=3$ ps. Shown near $t_D=0$ in the upper trace is the integral of the laser cross-correlation.

nonlinear least-squares fit to many data sets yielded $\tau=3$ ps, with no significant differences between the two probe wavelengths. Values of τ less than 2.2 ps or greater than 3.8 gave fits that looked poor, and the goodness-of-fit parameter, χ^2 , became much larger than its minimum value. Fitting with a sum of exponentials, $\text{LIF}(t_D) = \sum_i c_i [1-\exp(-t_D/\tau_i)]$, did not decrease χ^2 by more than two percent, so given the present signal-to-noise ratio, the data were fit by a single risetime. The laser pulse durations in this experiment are much shorter than the reaction time, so deconvolution of the pulse duration is unimportant. Also shown in Fig. 1 is the numerical integral of the experimental cross correlation, which would be the LIF time dependence if the transition state were very short lived.

It seems reasonable to interpret the observed 3 ps risetime of OH as being the decay time of a CH₃OH* intermediate (cf. also Refs. 18-21). The dissociation, $O_3 + h\nu_{267 \text{ nm}} \rightarrow O(^1D_2) + O_2(^1\Delta_g)$ is prompt²³⁻²⁵ ($\tau_{\text{DISS}} < 15$ fs) and the average kinetic energy release^{26,27} is ~4550 cm⁻¹ (O atom velocity of $\sim 2.1 \text{ nm ps}^{-1}$), so a direct process, not involving a long-lived intermediate, should be very fast. Furthermore, the value of 3 ps is comparable to the lifetime calculated from Rice-Ramsburger-Kassel-Marcus (RRKM) theory for the dissociation of methanol at the level of excitation of these experiments. The RRKM lifetime, calculated²⁸ using the vibrational frequencies and rotational constants for the CH₃OH activated complex determined by Tsang² to reproduce the experimental thermal rate constant parameters for the reaction $CH_3OH \rightarrow CH_3 + OH$, is ~2 ps for an energy, E^{\dagger} , 16 500 cm⁻¹ above the thermodynamic threshold $(E^{\dagger} = \Delta H + E_{\text{trans}} = 14\ 980 + 1515\ \text{cm}^{-1})$. Agreement with an RRKM calculation at a single energy is not definitive, and until τ has been measured for many energies and H/D isotopic substitution experiments are completed, one may only claim that the present results are consistent with statistical theory.

One may question whether the dynamics in the cluster

are a fair model for those of the analogous "free" or bimolecular reaction, $CH_4+O({}^1D_2)$. The observed¹⁴ rovibrational distribution, P(v,J), for nascent OH formed from the $CH_4 \cdot O_3$ clusters is almost identical to the P(v,J) of the free reaction.⁹ This suggests that the presence of the O_2 as a third body in the complex does not radically influence the energetics and that there is a similar reaction mechanism for the cluster and free reactions. Since almost all of E^{\dagger} arises from the reaction exothermicity, not the kinetic energy from ozone photolysis, reduction of E^{\dagger} due to a "squeezed atom" effect^{19,20} is unimportant. Additionally, P(v=0,J) was measured using the fast photolysis laser and a high resolution probe laser and found to be indistinguishable from that measured using a ns photolysis laser.¹⁴

From the classical chemical quenching experiments^{1,2} a lifetime for the CH₃OH* intermediate of 0.8 ps was deduced. This value was the slope-to-intercept ratio of N₂/CH₃OH vs CH₄ pressure following photolysis of nitrous oxide, N₂O+ $hv_{185 \text{ nm}} \rightarrow N_2 + O(^1D_2)$. A significant correction for the putative unquenchable fast channel was made to the data, and an E^{\dagger} -independent quenching rate constant of 2×10^{11} M⁻¹ s⁻¹ (3×10^{-10} cm³ s⁻¹) was assumed to deduce the 0.8 ps value. As discussed by Tsang,² these experiments¹ did not determine whether the O($^{1}D_{2}$) was thermalized prior to reaction, thereby creating an uncertainty up to 7800 cm⁻¹ in the energy content of the CH₃OH*. Because of these uncertainties and the different nature of the two experiments, the difference between 0.8 ps and the 3 ps reported here is not surprising.

In addition to OH from the long-lived CH₃OH* complex, in the free reaction a major fraction of the OH was hypothesized to be formed via a short-lived intermediate that is not quenched in the classical chemical studies. In the laser studies⁷⁻¹³ of OH product P(v,J), this prompt channel supposedly yields OH in high rovibrational states and accounts for most of OH formed. OH(v=0) even in low rotational states is from the RRKM-like reaction channel.⁹ While the spectral breadth of a fast laser does not permit probing a single rotational level, the OH rise times at 308.0 m (mostly low-J) and 306.1 nm (mostly high-J) are the same. No evidence was seen for a fast OH component. Given the time resolution and signal-to-noise of these experiments, any prompt OH channel must produce less than 13% of the OH probed at 308.0 nm and less than 20% of that probed at 306.1 ns.²⁹ It is conceivable that vibrationally excited OH produced in rovibrational states not yet probed is formed through a short-lived intermediate.

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- ²⁹Recent analyses of OH(v=0,N=5) Doppler profiles for the $CH_4+O(^{1}D_2)$ bimolecular reaction indicate a persistent intermediate complex for that product channel (private communication, J. P. Simons).