

A crossed molecular beam study of the $O(^1D_2) + CH_4$ reaction

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The reaction of $O(^1D_2)$ with methane has been a matter of considerable interest.¹ UV photolysis of N_2O-CH_4 or O_3-CH_4 mixtures has been used to study this reaction in gas phase²⁻⁶ and also in a liquid argon medium.⁷ Lin and DeMore,⁶ in an extensive gas phase study, have identified four primary reactions, (1) $O(^1D) + CH_4 \rightarrow CH_3 + OH$, (2) $O(^1D) + CH_4 \rightarrow H_2 + HCHO$, (3) $O(^1D) + CH_4 \rightarrow CH_3OH^* \rightarrow CH_3 + OH$, and (4) $O(^1D) + CH_4 \rightarrow CH_3OH^* \rightarrow CH_3O + H$. The production of OH, reactions (1) and (3), constitute 80% of the yield, the direct molecular H_2 elimination is about 9%, and reaction (4), hydrogen atom elimination is less than 2%. We have performed a crossed molecular beam investigation of this reaction using a supersonic $O(^1D)$ beam source developed in our laboratory.⁸ Our results show that, in fact, hydrogen atom elimination, reaction (4), greatly exceeds molecular hydrogen elimination which is not observed to occur appreciably.

The $O(^1D_2)$ beam is crossed at 90° with a room temperature supersonic beam of CH_4 in a collision chamber maintained at $\sim 1 \times 10^{-7}$ Torr. Although the beam also contains $O(^3P)$, only $O(^1D_2)$ reacts with CH_4 appreciably at low collision energies.⁴ Reaction product angular distributions are measured by a triply differentially pumped rotatable quadrupole mass spectrometer, kept at $\sim 10^{-11}$ Torr in the ionization region.⁹ Product velocity distributions are determined by a cross correlation time-of-flight (TOF) technique.¹⁰ The reaction product was observed at mass 30 and 31. The mass 31 product can be identified with CH_3O (or CH_2OH) product. The mass 30 signal can arise either from direct production of formaldehyde or from fragmentation of the mass 31 product in the ionizer. In order to identify the mass 30 signal, angular and velocity distributions were obtained. Figure 1 shows the angular distribution of mass 30 product from the reaction of $O(^1D)$ with CH_4 at a collision energy of 6.4 kcal/mole. The mass 31 signal (not shown) is contaminated by a small fraction of the O_2 , mass 32, elastically scattered from the oxygen beam by the CH_4 . The elastic contribution can be separated from the reactive mass 31 signal in the time of flight (TOF) distributions. Shown in Fig. 2 is the TOF spectrum for mass 30 and 31 after correcting the latter spectrum by subtracting the mass 32 elastic contribution. The excellent agreement between the distributions is strong evidence that both masses are produced from a single reactive channel. The source of the mass 30 signal, then, is not a dynamically distinct channel, but is the ionizer fragmentation of the CH_3O (or CH_2OH) product. The intensity ratio of the mass 30 to 31 TOF spectra was found to be constant at different angles,

verifying that mass 30 and 31 are produced from the same species. Also consistent with this conclusion is the narrow angular distribution of mass 30 (Fig. 1) which would not be expected from the highly exoergic ($\Delta H = -113$ kcal/mole¹¹) $HCHO + H_2$ reaction with significant exit barrier. The most translationally energetic $m/e = 30$ product, if attributed to direct H_2CO formation, would contain less than 15% of the available energy. The H elimination channel can be accompanied by either CH_3O or CH_2OH radical formation, having slightly different exoergicities¹¹ (33 and 43 kcal/mole, respectively), but the two pathways cannot be distinguished in our experiment.

From the breadth of the product angular and velocity distributions, we estimate that the mean product translational energy is 15 kcal/mole. In the gas phase experiments, the translationally hot hydrogen atoms will react with CH_4 with very high cross section, producing H_2 at a much higher rate than would be expected assuming thermalized H atoms.

We have estimated our detection sensitivity for H_2 elimination by assuming a statistical product energy distribution for this channel and calculating the product distributions expected. From our failure to detect any evidence of molecular H_2 elimination we conclude that

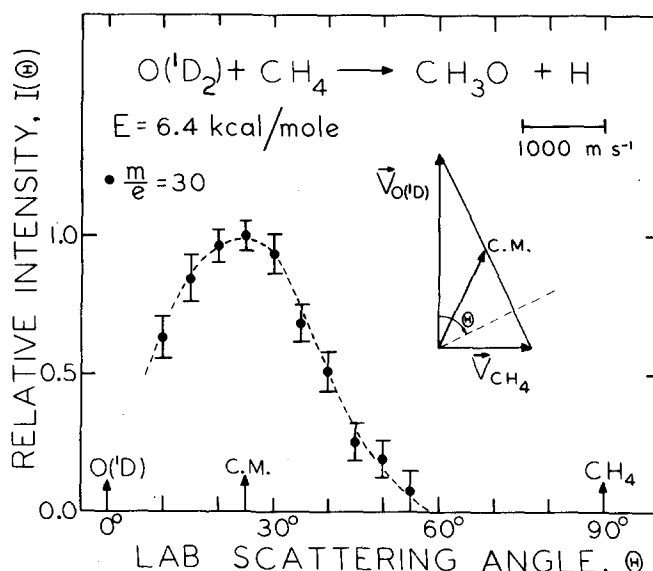


FIG. 1. Laboratory angular distribution from the $O(^1D_2) + CH_4$ reaction. The primary reaction product found was CH_3O (or CH_2OH), which subsequently fragmented in the ionizer. The dashed line is drawn through the data for clarity.

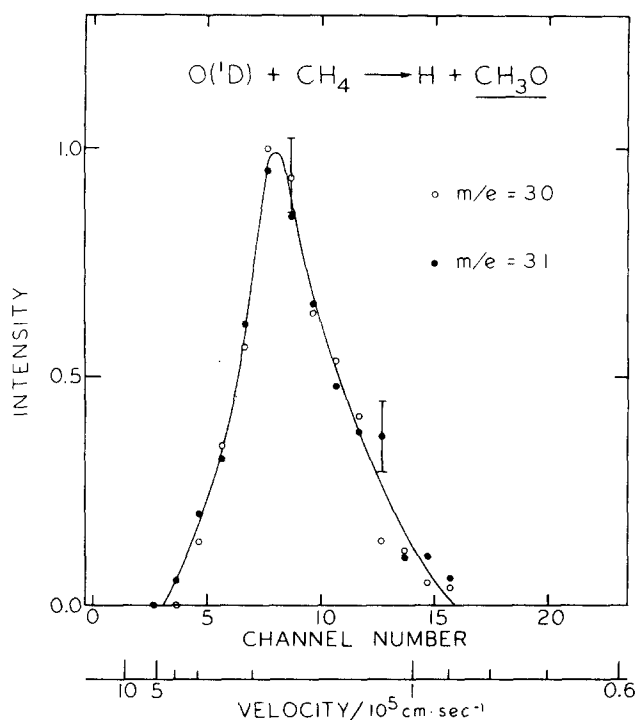


FIG. 2. Experimental TOF of mass 30 (○) and mass 31 (●). A line is drawn through the points for clarity. Error bars are typical of all points and represent 95% confidence limits.

reaction (2) is less than 25% of the H atom elimination under our reaction conditions.

This study has shown that the H atom substitution process greatly exceeds H_2 elimination in the reaction $O(^1D) + CH_4$. This result is in agreement with our rate calculations based on a recent *ab initio* study of the H_4CO potential energy surface¹² which found the barriers to H_2 loss from methanol producing hydroxymethylene,

94 kcal/mole and formaldehyde, 100 kcal/mole. With these barriers to H_2 molecular elimination, the simple CH bond cleavage was calculated to be the dominant process.

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On the determination from Raman spectra of the polarizability derivative with respect to the O–D bond stretching coordinate in the ices

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We denote by RP the ratio α_1/α_2 , where α_1 is the component parallel to the bond of the polarizability derivative with respect to the O–D bond stretching displacement of a water molecule, and α_2 is one of the two components, which are assumed equal, perpendicular to the

bond. Scherer and Snyder¹ found the value $RP = 5.6$ from a least-squares refinement of the relative integrated intensities, under various polarizations, of the bands due to O–H and O–D stretching modes of HDO molecules isolated in single-crystal, D_2O or H_2O , ice