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Kinetics of the reaction of O_2^+ with CH_4 from 500 to 1400 K: A case for state specific chemistry

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Rate constants and branching ratios have been measured for the reaction of O_2^+ with CH_4 over the temperature range from 500 to 1400 K. The rate constants increase dramatically over this temperature range, in good agreement with a previous study from our laboratory. A complex chemistry was found. The main product at low temperature, $CH_2O_2H^+$, disappears almost completely at high temperature, in part due to thermal dissociation. The main products at high temperature are CH_4^+ and HCO^+; the latter ion has not been observed previously. Also prominent at high temperature are H_3O^+ and CH_3^+. A small amount of CH_3O^+ is observed at all temperatures. H_2O^+ is observed in small quantities at high temperature. Branching ratios for the reaction of O_2^+ with CD_4 are also reported, confirming the ion assignments. Comparison to drift tube and beam results indicates that vibrational excitation of the CH_4 promotes several of these channels more than other forms of energy. Channels which proceed through the $t\text{-}CH_3OOH^+\ {}^2A''$ intermediate (described in the accompanying paper) are probably not strongly dependent on the form of energy, although uncertainties prevent a definitive conclusion. The charge-transfer channel and the channels requiring substantial rearrangement are greatly enhanced by vibrational excitation. Thus, specific channels do appear to be governed by vibrational excitation. [DOI: 10.1063/1.1352033]

INTRODUCTION

The reaction of O_2^+ with CH_4 was first observed by Franklin and Munson in 1965.[1] Since that time, there have been numerous studies of this reaction,[2–24] making it one of the most studied ion–molecule reactions. The main product at low temperature and kinetic energy is $CH_2O_2H^+$.[13,21] Studies as a function of translational energy have shown that increased translational energy promotes new channels such as CH_3^+ and CH_4^+.[10,21] In addition, we have found that vibrational excitation in CH_4 increases the overall reactivity dramatically.[22,23] In the previous experiments, it was not possible to test whether the CH_4 vibrational excitation increased the reactivity uniformly over all channels or specific channels were the cause of the increase. However, our high-temperature flowing afterglow (HTFA) has been recently modified to allow measurements of branching ratios up to 1400 K.[25,26] By making measurements as a function of temperature and then comparing to data previous drift tube or beam results, it is possible to examine whether vibrational excitation promotes specific channels.[27]

We have previously reported results for this reaction taken at 1400 K,[24] and these results were exceptionally surprising. Based on past drift tube work,[10] only three different product ions were expected. Instead, a rich chemistry was observed, including seven primary product ions, and two secondary products from 13 individual processes. Several of the channels involve breaking and forming up to four chemical bonds. In this paper, temperature dependent rate constants and branching ratios are presented from 500 to 1400 K for the reaction of O_2^+ with CH_4 and branching ratio only data for the O_2^+ reaction with CD_4. By comparing to previous studies, the influence on vibrational excitation in the CH_4 reactant is derived. Details of the potential-energy surface are presented in the accompanying paper.[28]

EXPERIMENT

The measurements were made in the high-temperature flowing afterglow, which has been described in detail previously.[25,26,29] Only details pertinent to the present study are given here. An industrial grade quartz flow tube was inserted into a three-zone commercial furnace. While the furnace can reach temperatures up to 1800 K, the quartz flow tube limited the present measurements to 1400 K. An electron impact ion source was located in the upstream end of the flow tube. The helium carrier gas was ionized and O_2 is added slightly downstream of the ionization region. Reactions of He^+ and He^* produced O^+ and O_2^+. However, sufficient O_2 was added to convert all the O^+ to O_2^+ before the CH_4 or CD_4 was added further downstream. The O_2^+ signal at temperatures of 500 K and above was very clean. At lower temperatures, impurities such as H_2O from the outgassing firebrick used in the furnace resulted in H_3O^+ and NO^+ being present. Thus, branching measurements were difficult below 500 K. O_2^+ ions comprise over 99% of all ions at 500 K and above, except for alkali ions emitted thermally from

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the hot flow tube walls. The alkalis were nonreactive and, therefore, did not interfere with the measurements. An example of a spectrum has been shown elsewhere.[24] The branching ratios were independent of the O_2 concentration, except that the charge transfer channel is scavenged by the O_2 as described below.

CH_4 or CD_4 was added about 30 cm downstream of the ion source, 50 cm from the sampling orifice. Signals were recorded as a function of the CH_4 flow. Normally, one extrapolates product branching fractions to zero reactant flow to obtain the primary branching ratios. However, the primary reaction was quite slow and some of the secondary chemistry was fast, making the zero extrapolation difficult to interpret. Extrapolations to infinite flow were also used. Nevertheless, all channels could only be separated at 1400 K. The separation is possible at high temperature because the overall rate constant is considerably larger, resulting in less CH_4 being added, which in turn makes secondary chemistry less important.

The mass spectrometer in the HTFA has little mass discrimination when using low-mass resolution and most of the data was taken under these conditions. For channels 1 AMU apart, the low resolution data were divided into individual peaks using higher resolution data. The rate constants are accurate to 25%, and relative errors are 15%.[29] The branching ratios are accurate to 25% except where noted.[30]

RESULTS AND DISCUSSION

Table I lists all the processes and potential processes that can occur in this system involving O_2^+, O_2, and CH_4. The thermodynamic data for all reactions listed are taken from the NIST Webbook,[31] from Van Doren *et al.*,[13] and from Fisher and Armentrout.[21] Reactions (1)–(7) are the primary channels observed in the present experiments. Reactions (5)–(7) have not been observed elsewhere, but HCO^+ has been reported as a charge injection device (CID) product of $CH_2O_2H^+$ dissociation.[16,32] Reactions (8) and (11) have been observed previously at high-kinetic energy[21] and reaction (9) at low temperature.[14] Thus, of all the possible channels, only reaction (10) has never been observed. We made a careful search for this channel and cannot rule out a small signal at high temperature. However, reaction (18) and a mass coincidence with $H^{13}CO^+$ and $C^{13}CH_5^+$ prevented a definitive determination. One might expect a small amount of H_2CO^+ since it is related to the H_2O^+ channel by charge location and to the CH_2OH^+ channel by proton transfer.

Many of the channels have mass coincidences, and several of the primary products react with either CH_4 or O_2 making quantification by normal means difficult. For example, $CH_2O_2H^+$ thermally decomposes above 1000 K. The evidence for the thermal decomposition is a decrease in the branching fraction at higher CH_4 flows. The large extent of reaction at large CH_4 flows results in an increase in the effective reaction time for secondary chemistry since more of the product is formed upstream. The primary reaction time is, of course, invariant. At all temperatures, the branching fraction for this channel is reported from the extrapolation to zero flow, corrected for products not detected at low flow. This underestimates the nascent branching ratio at high temperature by neglecting contributions from thermal dissociation, i.e., the reported branching ratios are lower limits.

TABLE I. Possible reaction channels for the O_2^+ plus CH_4 or CD_4 systems with O_2 present. Ion masses are listed both as actual mass and those observed in the experiment after secondary chemistry has occurred as described in the text. Thermodynamic data are taken from the NIST Webbook (Ref. 31), from Van Doren *et al.* (Ref. 13), and from Fisher and Armentrout (Ref. 21).

Reaction	Actual mass H(D)	Observed mass H(D)
Primaries observed		
(1) $O_2^+ + CH_4 \rightarrow CH_2O_2H^+ + H + 22$ kcal/mol	47(50)	47(50)
(2) $O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2 - 0.4$ kcal/mol	15(18)	29(34)
(3) $O_2^+ + CH_4 \rightarrow CH_4^+ + O_2 - 12.45$ kcal/mol	16(20)	17(22)
(4) $O_2^+ + CH_4 \rightarrow H_3O^+ + HCO + 113$ kcal/mol	19(22)	19(22)
[5(a)] $O_2^+ + CH_4 \rightarrow HCO^+ + H + H_2O + 69$ kcal/mol	29(30)	29(30)
[5(b)] $\rightarrow HCO^+ + OH + H_2 + 54$ kcal/mol		
(6) $O_2^+ + CH_4 \rightarrow CH_3O^+ + OH + 78$ kcal/mol	31(34)	31(34)
(7) $O_2^+ + CH_4 \rightarrow H_2O^+ + CH_2O + 53$ kcal/mol	18(20)	18
Primaries not observed		
(8) $O_2^+ + CH_4 \rightarrow CO_2^+ + 2H_2 + 37$ kcal/mol	44	
(9) $O_2^+ + CH_4 + M \rightarrow O_2^+(CH_4) + M$	48(52)	
(10) $O_2^+ + CH_4 \rightarrow CH_2O^+ + H_2O + 95$ kcal/mol	28(30)	
(11) $O_2^+ + CH_4 \rightarrow CH_2O_2^+ + 2H - 9.5$ kcal/mol	46(48)	
Secondary chemistry		
(12) $CH_4^+ + O_2 \rightarrow O_2^+ + CH_4$	32	
(13) $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	29(34)	
$\rightarrow C_2H_3^+ + 2H_2$	27(30)	
(14) $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	17(22)	
(15) $HCO^+ + CH_4 \rightarrow CH_5^+ + CO$	17(22)	
(16) $CH_3O_2^+ + He(CH_4) \rightarrow$ products	?	
(17) $H_2O^+ + CH_4 \rightarrow H_3O^+ + CH_3$	19(22)	
(18) $H_2CO^+ + CH_4 \rightarrow CH_3O^+ + CH_3$	31(34)	
$\rightarrow C_2H_5O^+ + H$	45(50)	

CH_3^+ reacts rapidly with CH_4 to produce $C_2H_5^+$ [reaction (13)],[33] which has the same mass as HCO^+. A small amount of $C_2H_3^+$ is also observed at 1400 K from the reaction of CH_3^+ with CH_4. It became clear that the mass 29 AMU signal is due to both HCO^+ and $C_2H_5^+$ only after studying the CD_4 reaction. In a previous flow tube study,[10] it was assumed that the signal at 29 AMU was due only to $C_2H_5^+$. The fast secondary chemistry of CH_3^+, coupled with the small primary reaction rate constant, prevents the HCO^+ and CH_3^+ channels from being separated. The sum of the two channels is, therefore, reported, except at 1400 K, where the overall primary reaction is fast enough to use an extrapolation to zero CH_4 flow. Limits can also be placed on the two channels at 1200 K. The overall rate constant at 1400 K is over ten times faster than the 500 K rate constant. Additional complications are that two potential sets of neutral products can accompany HCO^+ production and that HCO^+ has two isomeric forms. We list the ion as HCO^+ because CID has shown that $CH_2O_2H^+$ dissociates into HCO^+ not HOC^+ although we have no evidence as to which ion is formed.[32] We have no information concerning which of the two neutral product sets is formed either.

The charge-transfer channel is obscured at low CH_4 flow because of the back reaction with the O_2 source gas, reaction (12). At very large CH_4 flows, the rate for reaction (14) is much faster than that for reaction (12), and CH_4^+ is much

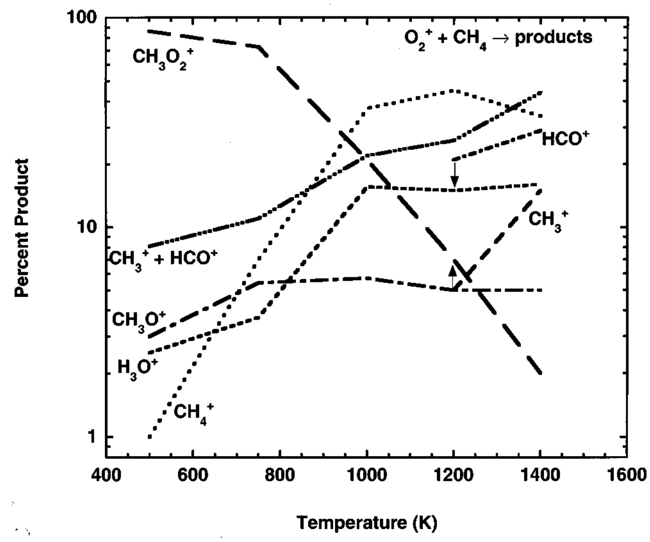

FIG. 1. Percent product vs temperature for the reaction of O_2^+ with CH_4. The CH_3^+ and HCO^+ points at 1200 K are shown as limits.

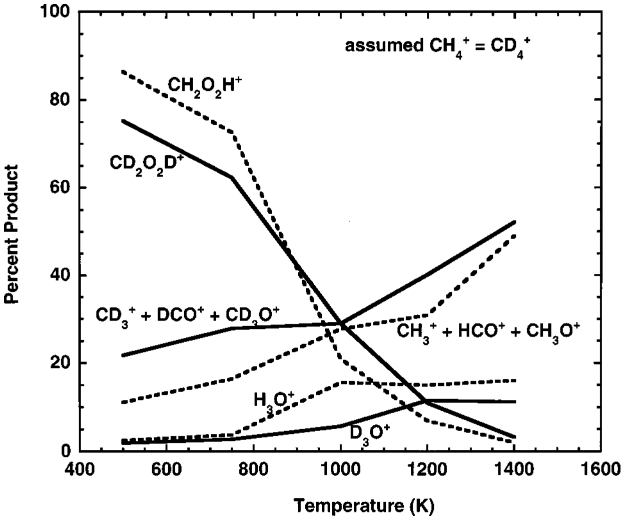

FIG. 2. Comparison of the percent branching for the reactions of O_2^+ with CH_4 and CD_4 vs temperature. Several channels are summed together. The percentage of CD_4^+ was assumed to be equal to that for CH_4^+; see text.

more likely to end up as CH_5^+ than O_2^+. The CH_4^+ branching fraction is taken as the CH_5^+ fraction at large CH_4 flows. Other channels, for which the zero flow extrapolation is used, are corrected for the charge-transfer channel obtained in this manner.

Determining the H_3O^+ channel is straightforward except that under most conditions any H_2O^+ produced converts to H_3O^+, due to reaction (17). At high temperature ($\geqslant$1000 K), we observe a small amount of H_2O^+ at very low CH_4 flows. While this signal is difficult to quantify we estimate it to be 10%–20% of the H_3O^+ fraction. At lower temperatures the small signals in these channels and the fast secondary chemistry prevents a meaningful search from being conducted.

Finally, low mass resolution settings obscure the CH_3O^+ channel, i.e., it is hidden in the large O_2^+ signal one AMU higher. The peak clearly stands out at large CH_4 flows where the O_2^+ is depleted, under higher resolution settings, or in the CD_4 experiments,. We report values taken at high depletions. Corrections to the data taken at low flow are made for this channel in the same way as for the CH_4^+ channel. We believe that previous studies probably missed this channel since we observe it at all temperatures.

Similar logic is used to unravel the CD_4 data. However, the mass coincidences are different, and we were restricted to low flows due to the cost of CD_4. A typical run with high flows uses several liters of CH_4, and the CD_4 rate is even slower.[11] Therefore, less information is obtained for the CD_4 reaction, which is used mainly to confirm the CH_4 results.

Product branching percentages for the CH_4 reaction are shown in Fig. 1 as a function of temperature. At low temperature, $CH_2O_2H^+$ approaches 100% of the reactivity although four or five other channels are observed in small abundance. The $CH_2O_2H^+$ channel decreases substantially at high temperature; only 2% is found at 1400 K, partly as a result of thermal decomposition. $CH_2O_2H^+$ was the main product observed in previous experiments, at least at low temperature or kinetic energy.[9,10,13,21]

At low temperature, the mass 29 signal, i.e., the sum of the CH_3^+ and HCO^+ channels, is the second most abundant signal. This sum increases to 46% of the reactivity at high temperature. At 1400 K, the two channels can be separated, and HCO^+ is twice as abundant as the CH_3^+ channel. A drift tube study of the collisional dissociation of $CH_2O_2H^+$ found that this ratio was 1.5 over an extended energy range.[32] In previous work, the HCO^+ channel had not been reported as a primary ion;[10,21] all ions at mass 29 were assumed to result from reaction (13). The HCO^+ channel is significantly exothermic while the CH_3^+ channel is approximately thermoneutral.

Charge transfer is 12.45 kcal/mol endothermic and the profile is consistent with an endothermic channel, i.e., increases rapidly with increasing temperature. At temperatures $\geqslant$1000 K, CH_4^+ is the most abundant channel, with a branching fraction leveling off near 40%. This channel has been observed previously at high-kinetic energies.[10,21]

The percentage of the CH_3O^+ channel is roughly constant at 3%–5%. This channel has not been observed elsewhere. We believe that is because of the mass overlap with the large primary peak as explained above. The H_3O^+ channel is 2% at 500 K and rises to 14% at 1400 K. The reported value includes a small contribution from H_2O^+, which is estimated to be ~10%–20% of the total mass 19 signal at temperatures $\geqslant$1000 K. H_3O^+ has been observed previously in lower abundance in the guided ion beam experiment and also as a product of collisional dissociation of the $CH_2O_2H^+$ ion in a drift tube.[32]

Figure 2 shows the branching percentages for the CD_4 reaction compared to the CH_4 reaction. As stated earlier, less information was obtained for the CD_4 reaction, due to the prohibitive cost of using large flows of CD_4. The main impetus for the CD_4 experiments was to check the identities of the previously unidentified products. In fact, only by performing the CD_4 experiments were the CH_3O^+ and HCO^+ channels found. No estimate of the amount of CD_4^+ produced could be made. Therefore, we assumed that the percentage of charge transfer in the CD_4 reaction was the same as that found in the CH_4^+ reaction. Although this is probably not accurate, it seems to be the best way to compare the two reactions. The two isotopic data sets show similar trends, however, some differences are observed. Less $CD_2O_2D^+$ is observed at low temperatures and more of the sum of the CD_3^+, DCO^+ and CD_3O^+ channels is found. Slightly less D_3O^+ is observed. While the rate constants for the CD_4 reactions were not measured, previous measurements show that they are significantly less than those for CH_4 at low temperatures.[11] Due to the quality of these data, it is hard to make any definitive judgements except to say that they confirm the trends and mass assignments found for the CH_4 reaction.

We have previously measured the rate constants for the overall reaction up to 1400 K.[22–24] The present results are in good agreement with those results. Total rate constants rise rapidly throughout the entire temperature range in this experiment. Previous results show the rate constants have a minimum at about 300 K and increase at low temperature.[9,22] Comparing temperature data and kinetic-energy data shows that the rate constants as a function of temperature increase more dramatically than when kinetic energy is increased. At 1400 K, the total rate constant is twice as large as that found in the guided ion beam at the same total energy. This shows that CH_4 vibrations promote reactivity more effectively than does translational energy.[22,23]

The main goal of the present study was to determine whether the increased reactivity was due to specific channels. The best way to test for this is to plot the rate constants for specific channels when temperature is increased compared to when translational energy is increased. Plotting the data as total energy (defined as the sum of the average rotational, translational, and vibrational energy of the reactants, excluding zero-point energy) allows one to easily compare whether different forms of energy behave similarly. Overlapping data indicate that all forms of energy behave similarly.

Figure 3 shows the rate constants for the $CH_2O_2H^+$, CH_3^+, and CH_4^+ channels as a function of total energy. Also shown are the data of Fisher and Armentrout[21] taken in a guided ion beam (GIB). The GIB data are approximated by taking several points from there graph and are similar to the drift tube results of Durup-Ferguson *et al.*,[10] which are not shown for clarity. Both of these studies refer to translational excitation, although in the drift tube the internal temperature of the O_2^+ is raised slightly through the collisions with the buffer gas.[34–36] The lowest energy point (500 K) for the $CH_2O_2H^+$ channel agrees with the translational energy results. The next HTFA point (750 K) is slightly higher than the translational energy point. At higher temperatures the reverse is found, i.e., the translational energy points are larger by a considerable amount. However, the higher temperature points include thermal dissociation of $CH_2O_2H^+$ by the helium buffer and, therefore, underestimate the nascent population. Due to the secondary chemistry it is not possible to accurately estimate the influence of this channel. It would require approximately about a factor of 3.5, 2.5, and 1.5 increase in this channel to bring the two data sets into agreement at 1400, 1200, and 1000 K, respectively. This is on the order of what we might estimate, although the exact amount of decomposition cannot be determined. In any case, after taking thermal dissociation into account, the difference between the data sets is smaller than what is found for several of the other channels and may in fact be approximately the same. This indicates that internal and translational energy affect the rate constant for this channel approximately equally. A small difference cannot be excluded.

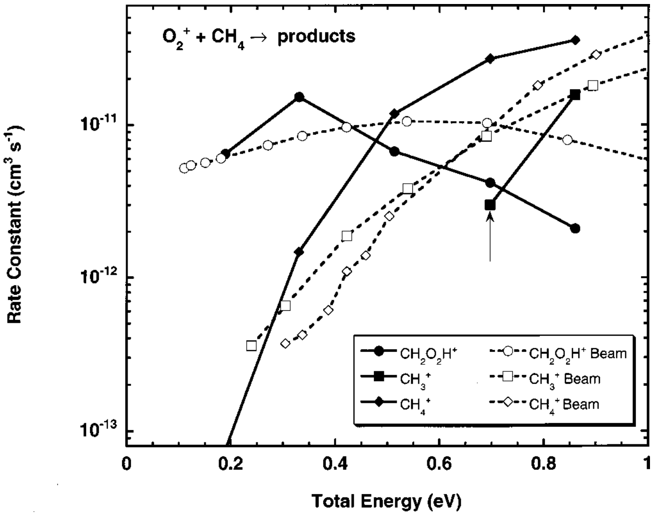

FIG. 3. Rate constants for the three main channels in the reaction of O_2^+ with CH_4 as a function of total energy. HTFA points are shown as solid symbols, and the GIB data from Fisher and Armentrout are shown as open symbols (Ref. 21). The drift tube data from Durup-Ferguson *et al.* are similar to the GIB data (Ref. 10). The CH_3^+ point at 1200 K is shown as a limit.

Charge transfer is endothermic by 12.45 kcal/mol. Both data sets show this channel increases with energy, as expected for an endothermic channel. However, the HTFA results are larger than the translational energy results over the entire energy range showing that vibrational energy promotes this channel. In other studies of this type, we have found that vibrational energy often promotes charge transfer.[27,37,38] Since this becomes the major channel at high temperatures, it contributes significantly to the fact that the overall rate constant is greater when temperature is raised than when only translational energy is increased. There is only one overlapping point for the CH_3^+ channel, and all data sets are in good agreement for that point.

Figure 4 shows the rate constants for the rest of the product channels. Included in this figure are the rate constants for the sum of the HCO^+ and CH_3^+ channels, which are considerably higher than the CH_3^+ only channel in either of the kinetic-energy experiments. In the drift tube experiment, the secondary chemistry is similar to that found in the HTFA; thus the channel that had been reported as due to only CH_3^+ is really the sum of the two channels. The guided ion beam experiment should not suffer from this problem since no secondary chemistry occurs. Therefore, the good agreement between the drift tube and GIB data for the CH_3^+ channel indicate that little HCO^+ is formed at elevated translational energies in the drift tube experiment. This implies most of the HCO^+ formed in the HFTA experiments is a result of internal excitation, presumably CH_4 vibrations. Since this is also a major channel at high temperature, it

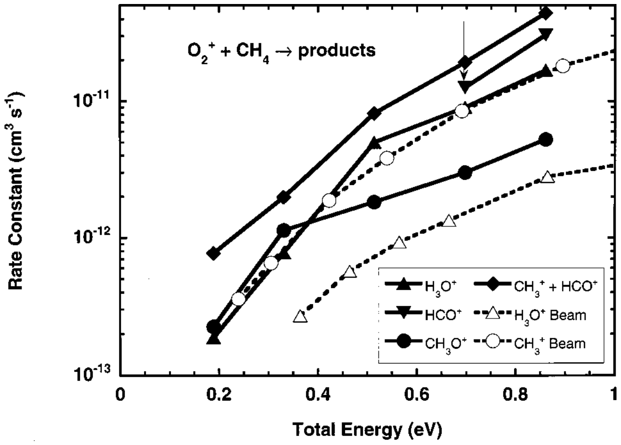

FIG. 4. Rate constants for the minor channels in the reaction of O_2^+ with CH_4 as a function of total energy. HTFA points are shown as solid symbols, and the GIB data from Fisher and Armentrout are shown as open triangles with a dashed-dotted line (Ref. 21). The HCO^+ point at 1200 K is shown as a limit.

contributes significantly to the overall increase in the rate constant compared to translational energy only.

The $H_3O^+ + HCO$ channel has the charge location reversed from the HCO^+ channel, and the rate constant is 5–7 times faster in the HTFA than in the GIB. Again, this is an indication that vibrational energy promotes this channel. Thus, both channels that form an HCO moiety (HCO and HCO^+) are enhanced by vibrational excitation. These channels require breaking three C–H bonds and the O_2 bond. It is not surprising that vibrational excitation would promote such extensive bond rearrangement. The HCO^+ channel is approximately a factor of 2 greater than the H_3O^+ channel at 1400 K, the only temperature where the HCO^+ channel can be separated from the CH_3^+ channel. More HCO^+ is formed than H_3O^+ even though the latter is considerably more exothermic. This may result from the entropy considerations, given that two neutrals are produced when HCO^+ is formed.

The CH_3O^+ channel has not been observed elsewhere. We believe this is an experimental artifact, and therefore no conclusion can be made about the effect of internal energy on this channel. CH_3O^+ is found to increase substantially with increasing energy. The calculations shown in the accompanying paper indicate that this ion probably has a CH_2OH^+ structure.

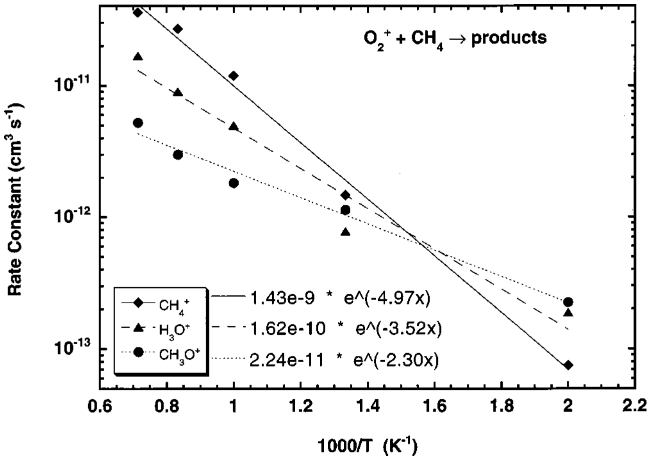

FIG. 5. Arrhenius plot for the CH_4^+, H_3O^+, and CH_3O^+ channels for the reaction of O_2^+ with CH_4.

Figure 5 shows an Arrhenius plot for the CH_4^+, H_3O^+, and CH_3O^+ channels. For all three channels the data are approximately linear although some scatter is observed. The activation energies are 9.9, 7.0, and 4.6 kcal/mol, respectively. The CH_4^+ activation energy is slightly lower than the endothermicity of 12.45 kcal/mol, indicating the efficiency for this channel is high once enough energy is available. This is reinforced by the pre-exponential factor being approximately equal to the collision rate constant of $1.15 \times 10^{-9}\ cm^3\,s^{-1}$. The other two channels are exothermic, and the Arrhenius-type behavior indicates the presence of barriers. The nature of several of the barriers is discussed in the companion paper. The sum of the HCO^+ and CH_3^+ channels roughly parallels the H_3O^+ channel ($E_a = 6$ kcal/mol), a further indication that these channels are related.

CONCLUSIONS

The present results show a much more varied story than has previously been found for this reaction. The reaction pathway shown in the companion paper[28] is quite convoluted. For the formation of the primary low-temperature product, $CH_2O_2H^+$, all barriers are below the energy of the reactants. However, the barrier to formation of a chemical intermediate is quite tight, i.e., restrictive. This results in the overall rate being very slow. An ion-induced dipole complex is easily formed, and this complex has been detected previously.[14] After passing this tight barrier, the complex goes through another more easily accessed four-member transition state to form the very stable t-$CH_3OOH^+\ {}^2A''$ complex. Several of the products observed in this study can be traced to this intermediate. Cleavage of one of the CH_3 hydrogens produces $CH_2O_2H^+$, the main low-temperature product. This happens without a barrier. CH_3^+ is formed from the t-$CH_3OOH^+\ {}^2A''$ intermediate by cleavage of the C–O bond. This channel proceeds through a barrier above the energy of the reactants. A direct pathway, i.e., one not involving a complex, from the reactants, with approximately the same barrier height as the pathway from the t-CH_3OOH^+ ${}^2A''$ intermediate, also leads to CH_3^+ production. The t-$CH_3OOH^+\ {}^2A''$ intermediate can also cleave an O–O bond, leading to CH_3O^+, which continues to rearrange to CH_2OH^+. This channel has a slightly larger barrier than that for the CH_3^+ channel. This is consistent with CH_3^+ being more abundant than the CH_2OH^+ channel. A comparison to activation energies is not possible since the CH_3^+ channel can only be separated from the HCO^+ channel at 1400 K. The activation energy for the CH_2OH^+ channel is in substantially smaller than the calculated barrier (14.7 and 4.6 kcal/mol for theory and experiment, respectively).

In both the beam and HTFA experiments, the $CH_2O_2H^+$ rate constant decreases at high energy with the decrease being more precipitous in the present experiments. Part or all of the difference is due to thermal decomposition of the $CH_2O_2H^+$ ion, and it is therefore difficult to really compare

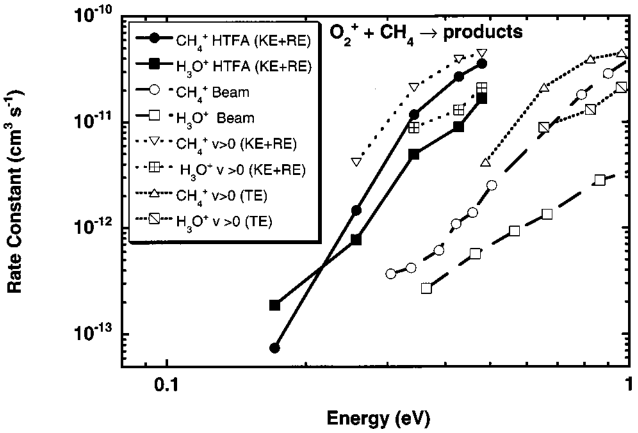

FIG. 6. Rate constants for the CH_4^+ and H_3O^+ channels in the reaction of O_2^+ with CH_4 as a function of energy. HTFA points are shown as solid circles and squares as a function of translational plus rotational energy. The GIB data from Fisher and Armentrout are shown as open circles and squares as a function of translational plus rotational energy. This also represents the data vs total energy since no vibrations are excited (Ref. 21). Inverted triangles and squares with plusses are derived rates for $v>0$ as a function of translational plus rotational energy. Triangles and squares with slashes are derived rates for $v>0$ as a function of total energy.

how different forms of energy effect this channel. The CH_3^+ channel agrees well with the beam data at 1400 K, the only point at which the HTFA results could be completely separated. The CH_3O^+ product was probably missed in the previous experiments due to incomplete mass separation, so it is not possible to separate the energy effects in this channel. Given the present uncertainties in these three channels, it is possible that they are governed by a total energy effect. In any case, the differences appear to be small compared to those observed for the other channels.

Charge transfer is observed to occur readily once sufficient energy is available and, therefore, does not appear to involve any barriers. More charge transfer is observed at the same total energy in the HTFA experiments than in the kinetic-energy experiments, indicating that vibrational excitation promotes this channel. This is based on the observation that rotational energy and translational energy were found to be equivalent at low temperature in controlling the total rate constants.[22] The activation energy (10 kcal/mol) is in reasonable agreement with the endothermicity (12.4 kcal/mol).

It is possible to derive rate constants for an average vibrational state.[27] If one assumes that the low-energy trend of the equivalency of rotational and translation energy continues, the best way to derive the vibrational effect is to plot the rate constants vs average rotational and translational energy. Figure 6 shows such a plot for this channel and the H_3O^+ channel. The beam data can be regarded as the $v=0$ rate constants and can be considered plotted vs either total energy or average rotational and translational energy since little vibrational excitation occurs. The derived rate constants for $v>0$ at the same average rotational and translation energy are 20–50 times larger than the $v=0$ rate constants (beam data). Adding the vibrational energy to the $v>0$ rates results in rate constants that are about a factor of 2 to 3 higher than the $v=0$ ones. Rate constants for individual vibrational modes may be expected to be very different from the average values derived. Increases such as those found for the $v>0$ compared to $v=0$ are often due to more favorable Franck–Condon overlap. The CH_4^+ ion is nonsymmetrical,[28] and therefore, asymmetrical vibrations may be expected to enhance this channel.

The other three channels that are observed, namely H_3O^+, HCO^+, and H_2O^+, are related in that they differ either by the position of the charge or by a proton. These channels require substantial rearrangement, a net result of forming and breaking three or four chemical bonds. The stationary points for these channels were not calculated in the accompanying paper. The rate constants for the H_3O^+ channel are 3–6 times higher in the present experiments than the beam experiments at the same total energy. HCO^+ and H_2O^+ have only been observed in this study. Thus, all three are substantially enhanced by internal excitation in the CH_4 since O_2^+ vibrations have not been observed to promote these channels.[10] Again, we derive rate constants for an average vibrational state, which are plotted in Fig. 6. This indicates vibrational excitation enhances this channel a factor of 30–40 over the $v=0$ rate at the same rotational plus translational energy. At the same total energy, the rates for vibrationally excited CH_4 are a factor of 6 to 7 times larger than the rate constants for the ground state.

The goal of this study was to determine how much of the vibrational enhancement in the rate constant for the O_2^+ reaction with CH_4 was due to specific channels. The results indicate that, for the channels going through the t-CH_3OOH^+ $^2A''$ intermediate, all forms of energy may be roughly equivalent, assuming much of the difference in the $CH_2O_2H^+$ channel is due to thermal dissociation by the helium buffer gas. In any case, the $CH_2O_2H^+$ channel diminishes with vibrational energy, and therefore, the increase in the rate constant is due to other channels. The charge-transfer channel and the three channels that result from the most bond rearrangement are all enhanced substantially by vibrational excitation. Thus, several channels can be described as being completely or mainly produced by vibrationally excited molecules, i.e., state selected chemistry.

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