Ion−Molecule Branching Ratios at High Temperature: Vibrational Energy Promotes Formation of New Channels in the Reaction of O_2^+ with CH_4

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Abstract: A High-Temperature Flowing Afterglow (HTFA) instrument has been modified to allow measurements of ion−molecule branching ratios at temperatures above 700 K for the first time. The technique is capable of temperatures at least as high as 1400 K, and here we report the branching ratios for the reactions of O^{2+} with CH_4 and CD_4 measured at 1400 K (for the reaction of O_2^+ with CH_4, the rate constant was also measured). Comparison to work using drift tube and guided ion beam techniques shows that heating the CH_4 vibrations produces new reaction product channels and enhances others. In particular, HCO^+, CH_3O^+, and H_2O^+ products are seen for the first time, and the H_3O^+ product is much more intense in comparison with experiments on vibrationally cold CH_4. The previously observed products CH_3^+ and CH_4^+ are comparable to those found with vibrationally cold CH_4. We conclude that vibrational excitation promotes those channels which require extensive bond rearrangement. Vibrational energy is found not only to promote the new channels but also to enhance the overall reaction rate.

Introduction

High-temperature ion chemistry plays an important role in Earth's ionosphere,[1] in plasma processing of microelectronics,[2] in plasmas associated with atmospheric entry,[3] and in a variety of other situations involving high-temperature gases. Recent evidence even suggests that ion chemistry could potentially be employed to enhance hydrocarbon−air combustion by affecting ignition and flame propagation time scales.[4] Ion−molecule reactions help to govern the composition, extent of ionization, and concentration of free electrons in all of these cases, thereby influencing the effects caused by these plasmas, e.g., effects on radiowave propagation, plasma processing efficacy, etc. The understanding and modeling of these high-temperature plasmas require detailed knowledge of not only the overall chemical reaction rates involved but also the distributions of reaction products (branching ratios) that result from the various reaction pathways. While product branching ratios are critically important to understanding the overall high-temperature chemistry, they are exceedingly difficult to measure under truly thermalized conditions; previous measurements have been achieved only for temperatures of 700 K and below.[5]

To address the need for high-temperature kinetics data, we have recently modified the High-Temperature Flowing Afterglow (HTFA) instrument in our laboratory[6] so that branching ratios as well as rate constants can be measured. The apparatus is capable of operating at temperatures up to 1800 K with a ceramic flow tube. However, a limit of 1400 K applies to the quartz tube used for the present studies. The reaction of O_2^+ with CH_4 is one of the most studied ion−molecule reactions[7−29] and a previous high-temperature study in our laboratory has shown that vibrational excitation dramatically increases the rate

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constant for this reaction.[28] While the rate constant for the overall reaction has been measured over a very wide temperature range (20−1300 K),[15,28,29] the product distribution of the reaction has been measured above room temperature only in nonthermal experiments. Those experiments show new channels appear at higher energy. Therefore, it is of interest to see whether the enhanced reactivity is due to specific channels or is a more general enhancement. These measurements along with other very recent measurements in our laboratory are the first branching ratio measurements for ion−molecule reactions measured above 700 K.[30,31]

In this paper, we report the branching ratios at 1400 K for the reactions of both CH_4 and CD_4 with O_2^+. In addition, the rate constant for the CH_4 reaction was measured. To our surprise, we observed three channels not previously reported. In addition, we observed enhanced reactivity at 1400 K in other channels, indicating that vibrational energy not only increases the overall rate but also leads to new pathways. A full report on the complete temperature dependence along with detailed quantum mechanical calculation of the potential surface will be published elsewhere.

Experimental Section

The HTFA has been described in detail elsewhere,[6] and only limited details will be given here. The apparatus in most respects is similar to a standard flowing afterglow.[32] For these experiments, an industrial grade quartz flow tube is inserted into a 3-zone commercial furnace. Reactions can be studied from 300 to 1400 K with the quartz flow tube. Ions are created by ionizing the helium buffer and adding sufficient O_2 to react with all of the He^+ ions and He* metastable atoms, forming O^+ and O_2^+. The O^+ ion reacts with O_2 to form O_2^+. In the past, impurities from outgassing fire brick and diffusion between the flow tube and the vacuum box surrounding the flow tube made branching ratio determinations difficult. The addition of a second large Roots blower on the vacuum box has largely solved this problem. Below 500 K, impurity ions can still be a problem. Ion signals of parent ions from the source gas can now be made with a purity of 99 to 99.9% (excluding nonreactive alkali ions formed from thermionic emission from surfaces). The addition of extra pumping has allowed branching ratios to be measured for the first time.

Figure 1 shows an example of the simplicity of the mass spectra. With no added CH_4, the spectrum is very clean; the dominant peak is K^+, followed by O_2^+ and Na^+. The only reactive impurity ion is a very minor O^+ signal (∼0.25% of the O_2^+ peak). The ability to produce a primary ion cleanly allows the branching ratio determinations. Without the addition of the large pump to the vacuum chamber, a “clean” spectrum typically showed impurities on the same order as that of the primary ion.

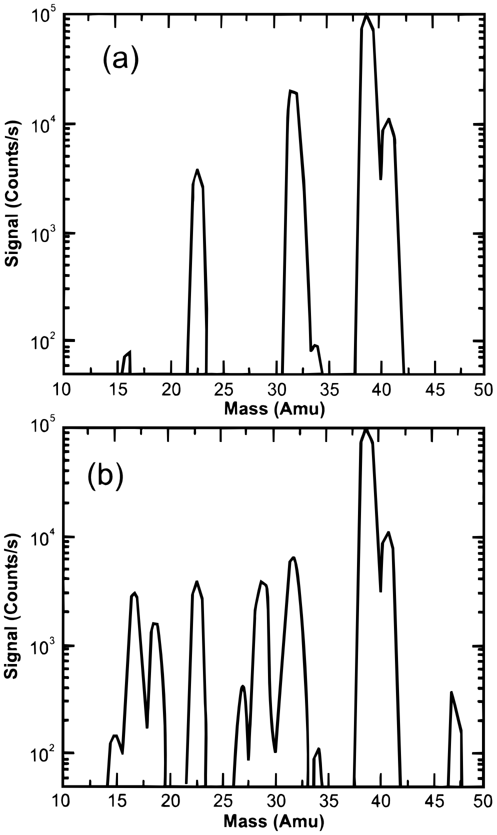

Figure 1. Low-resolution mass spectra taken without (a) and with (b) the addition of CH_4.

Results and Discussion

The chemistry of the O_2^+ reaction at 1400 K is quite complex. At room temperature and below, it is known that the reaction proceeds mainly by a bond insertion process to form $CH_2O_2H^+$,[19]

$$O_2^+ + CH_4 \rightarrow CH_2O_2H^+ + H + 22\ \text{kcal/mol} \qquad (1)$$

The thermodynamic data for all reactions listed are taken from the NIST Webbook,[33] from Van Doren et al.,[19] and from Fisher and Armentrout.[27] We expected to observe mainly two other channels since both drift tube[9,13] and beam[27] experiments have shown that at slightly elevated kinetic energies, two other slightly endothermic reaction channels grow in substantially,

$$O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2 - 0.4\ \text{kcal/mol} \qquad (2)$$

$$O_2^+ + CH_4 \rightarrow CH_4^+ + O_2 - 12.45\ \text{kcal/mol} \qquad (3)$$

In the beam experiments, three more channels were observed at high energies and were therefore expected to be of minor importance in the present thermal experiments.

$$O_2^+ + CH_4 \rightarrow CH_2O_2^+ + (2H) - 9.5\ \text{kcal/mol} \qquad (4)$$

$$O_2^+ + CH_4 \rightarrow H_3O^+ + HCO + 113\ \text{kcal/mol} \qquad (5)$$

$$O_2^+ + CH_4 \rightarrow CO_2^+ + (2H_2) + 356\ \text{kcal/mol} \qquad (6)$$

The last two channels are quite exothermic but were found to be minor pathways in the beam experiment, indicating that

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barriers exist. The barriers are presumably due to the extensive rearrangement necessary. The only other pathway previously observed[20] was a clustering channel at very low temperature.

$$O_2^+ + CH_4 + M \rightarrow O_2^+(CH_4) + M \tag{7}$$

In addition to the seven previously observed channels observed, a number of other exothermic product pathways are possible:

$$O_2^+ + CH_4 \rightarrow H_2O^+ + CH_2O + 53\ \text{kcal/mol} \tag{8}$$

$$O_2^+ + CH_4 \rightarrow CH_2O^+ + H_2O + 95\ \text{kcal/mol} \tag{9}$$

$$O_2^+ + CH_4 \rightarrow HCO^+ + H + H_2O + 69\ \text{kcal/mol} \tag{10a}$$

$$O_2^+ + CH_4 \rightarrow HCO^+ + OH + H_2 + 54\ \text{kcal/mol} \tag{10b}$$

$$O_2^+ + CH_4 \rightarrow CH_3O^+ + OH + 78\ \text{kcal/mol} \tag{11}$$

Furthermore, several of the ions are known to react with CH_4 to produce secondary reaction products; the processes involved are

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \tag{12}$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \tag{13}$$

In contrast to the simple chemistry expected from past measurements, we observed most of these products, i.e., all channels except reactions 4, 6, 7, and 9. In addition, we found the following interfering reactions to occur:

$$CH_4^+ + O_2 \rightarrow CH_4 + O_2^+ \tag{14}$$

$$CH_2O_2H^+ + He \rightarrow \text{thermal dissociation products} \tag{15}$$

$$H_2O^+ + CH_4 \rightarrow H_3O^+ + CH_3 \tag{16}$$

$$CH_3^+ + CH_4 \rightarrow C_2H_3^+ + 2H_2 \tag{17}$$

This reaction system, which is simple at room temperature and slightly more complex at elevated energies, is remarkably complex at 1400 K, with 13 processes occurring. Product ions were observed at nine masses, with two species at one of the masses. The product ions are found at 15 (CH_3^+), 16 (CH_4^+), 17 (CH_5^+), 18 (H_2O^+), 19 (H_3O^+), 27 ($C_2H_3^+$), 29 (HCO^+ and $C_2H_5^+$), 31 (CH_3O^+), and 47 ($CH_2O_2H^+$) amu.

Sorting out the chemistry could not be done by standard methods due to the secondary and interfering reactions. Branching ratios are derived normally by plotting the percent product vs reactant flow rate and extrapolating to zero flow rate to take into account secondary reactions. However, when the secondary chemistry is much faster than the primary reactants this becomes problematic. In the present case, reactions 14 and 15 caused further problems. In addition, some of the products, namely H_2O^+ and CH_3O^+, occur in the mass spectrum near much more intense peaks, and the resolution of our mass spectrometer is limited. Last the complication of HCO^+ and $C_2H_5^+$ having the same mass must be accounted for. In fact, the presence of the HCO^+ channel was only discovered during the CD_4 experiments.

An example of low-resolution mass spectra at moderate CH_4 flows is shown in Figure 1b. Here CH_3^+ (primary), CH_5^+ (secondary), H_3O^+ (primary), $C_2H_3^+$ (secondary), HCO^+ (primary) and $C_2H_5^+$ (secondary), and $CH_2O_2H^+$ (primary) products are evident. In addition, the CH_3O^+ product is evident as a low mass shoulder on the larger O_2^+ peak. By extrapolating data such as shown in Figure 1b to zero CH_4 flows, the 15:19:29:47 primary product ratio was determined. The mass $CH_2O_2H^+$ ion disappears at high flows due to thermal dissociation, and we use the low flow extrapolation without correction. We estimate that at most 4% of this product would be observed without thermal dissociation. We could not tell which product was the result of the decomposition, and therefore at least one of the other channels has a small error associated with this process. The low-resolution conditions resulted in good mass balance between product ion production and reactant ion loss, and no discrimination correction was needed.

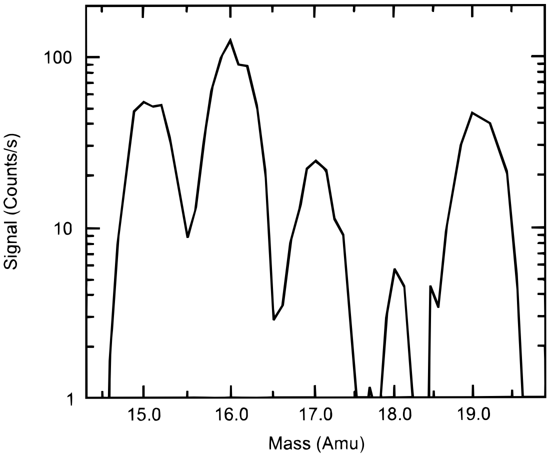

Figure 2. High-resolution spectrum over the 14−20 amu mass range at low CH_4 flow.

Three more product channels were observed and were quantified as follows. The H_2O^+ to H_3O^+ ratio could not be determined at low resolution since high-resolution conditions that result in mass discrimination were needed to separate the small 18 amu peak from the large 17 and 19 amu peaks. An example of a high-resolution spectrum from 14 to 20 amu is shown in Figure 2. The spectrum was obtained at low CH_4 flows over about 15 min. Due to the low signals that resulted from the high-resolution spectra, no extrapolation to zero flow was possible to account for reaction 16. The H_2O^+ to H_3O^+ ratio was taken as the average ratio of the peak heights in several spectra of this type. The lack of extrapolation is not a major problem as evidenced by the large 16:17 amu ratio, the 17 amu peak results from a fast secondary reaction.

The CH_3O^+ branching fraction was taken by adding large quantities of CH_4 so that the O_2^+ signal was sufficiently depleted so as not to interfere with the CH_3O^+ signal. The constant branching ratio at large CH_4 flows showed that CH_3O^+ was unreactive with CH_4. The large adjacent O_2^+ peak may therefore explain why the CH_3O^+ channel was not previously observed.

Finally, the CH_4^+ product branching fraction was also derived at large flows where the secondary reaction of CH_4^+ with CH_4 (forming CH_5^+) is faster than the reaction of CH_4^+ with O_2. Thus, the CH_5^+ signal at high CH_4 flows is a good measure of the amount of CH_4^+ formed. We estimate that the relative uncertainty in the product ratios is 15% except for the $CH_2O_2H^+$ channel, for which the nascent distribution could be twice as large as reported.

The main impetus for using CD_4 was to confirm mass assignments, in particular to confirm that the H_3O^+ ion did not

Table 1. Product Branching Percentages for the Reactions of O_2^+ with CH_4 and CD_4 at 1400 K[a]

product	branching, %		beam (0.86 eV)
	CH_4; *k*	CD_4[b]	
CH_3^+	15; 1.6(−11)	>16 ($CD_3^+ + CD_3O^+ = 22$)	28; 1.5(−11)
CH_4^+	34; 3.6(−11)	34 (assumed)	45; 2.4(e−11)
H_2O^+	2; 1.7(−12)	see H_3O^+	not observed
H_3O^+	14; 1.5(−11)	11(includes H_2O^+)	5; 2.7(−12)
HCO^+	29; 3.0(−11)	30	not observed
CH_3O^+	5; 5.3(−12)	<6% ($CD_3^+ + CD_3O^+ = 22$)	not observed
$CH_3O_2^+$	2; 2.1(−12)	3	15; 7.9(−12)
$CH_2O_2^+$	not observed		7; 4.0(−12)
total *k*	1.05(−10)		5.4(−11)

[a] The branching percentages are converted to rate constants for the CH_4 reaction by multiplying by the total rate constant. Data from a previous beam experiment on $O_2^+ + CH_4$ are shown at the same average total energy, 0.86 eV.[27] [b] Percent CD_4^+ assumed to be equal to that of CH_4^+.

result from an H_2O outgassing impurity. The mass shifted to 22 amu as expected. In addition, the CD_4 experiments were useful in finding the HCO^+ channel since $C_2H_5^+$ shifts by 5 amu and HCO^+ by only 1. The identity of the CH_3O^+ ions was also confirmed.

The quantity of CD_4 needed to derive the products which are best detected at high flow rates was prohibitively expensive. Therefore, less information was derived in the isotopically labeled experiment. Different mass coincidences occurred, and it was not possible to separate the CD_3^+ and CD_3O^+ channels. The CD_4^+ channel was taken to be the same as the CH_4^+ so that branching ratios for CH_4 and CD_4 could be compared. No rate constants were measured. The CD_4 data have larger errors compared with the CH_4 data due to the limited amount of data taken.

The measured branching ratios are shown in Table 1 along with rate constants for the CH_4 reactions obtained by multiplying the branching fractions by the overall rate constant. Within error, the branching ratios for the CD_4 and CH_4 systems are equal, with the assumption that the charge transfer channels are the same. Several of the products have been observed previously. Three of the products observed in the present experiments, namely HCO^+, CH_3O^+, and H_2O^+, have never been observed before from this reaction, and a fourth, H_3O^+, is seen in much greater abundance than was previously reported. These four channels comprise half of the reactivity at 1400 K. The most complete set of data to compare to is from Armentrout and colleagues,[27] taken in a guided ion beam apparatus. The beam data measured at the same total energy as the 1400 K HTFA data are listed in Table 1 for comparison.[27] To obtain total energy, the average rotational and vibrational energy calculated according to standard statistical mechanics formulas are used. Zero-point energy is the same in all experiments and is neglected.

From Table 1, it is clear that heating the reactants has a different effect on reactivity than does adding energy through translational energy. In particular, much more reactivity is found in channels that involve extensive bond rearrangement, while the rate constants for the CH_3^+ and CH_4^+ product channels are comparable in the two experiments. The H_3O^+ and HCO^+ product channels differ mainly by the location of the charge (in the latter case the corresponding H_3O neutral must decompose into OH plus H_2 or H_2O plus H). Both of these ionic channels involve breaking and making four chemical bonds. Coincidentally, the main low-temperature product channel was originally identified incorrectly as protonated formic acid,[11,12] a product that also requires the making and breaking of four bonds. This incorrect assignment inspired much of the interest in the reaction due to the complex rearrangement that was necessary. It is therefore somewhat ironic that the present results show that the H_3O^+ and HCO^+ channels comprise 43% of the reactivity at 1400 K. In contrast, these channels comprise only 5% of the reactivity at the comparable beam energy. The H_3O^+ channel proceeds 5.4 times faster in the HTFA experiment than in the beam, and HCO^+ was not observed. Neither of these channels was observed in the drift tube experiments.[9,13]

By process of elimination, the large enhancement in the pathways involving extensive bond rearrangement must be due to vibrationally excited CH_4. Rotational energy at low temperature has little effect on total reactivity, at least no more than does translational energy, and therefore is not expected to play a major role in controlling the reactivity at high temperature.[28] Vibrational energy in the O_2^+ has been found to promote mainly the $CH_2O_2H^+$ channel, with the CH_3^+ and CH_4^+ channels being promoted equally by translational and vibrational energy.[16,21,27] These three channels are the only ones that were observed in the experiments on vibrationally excited O_2^+. Comparing the beam data to the present results shows that all forms of energy affect these three channels approximately equally.

We have found previously that a single quantum in either of the two low-frequency vibrational modes of CH_4 enhances the overall reactivity by a factor of 17 compared with $\upsilon = 0$.[28] This increase at 500 K is about a factor of 10 larger than that found by adding the equivalent amount of translational kinetic energy. The total rate constant at 1400 K is 9% of the collisional value and about twice as large as that found in the beam experiment at the same total energy. Therefore, the CH_4 vibrations have a strong influence on both the overall rate constant and the branching ratios. Only 20% of the CH_4 molecules are in the ground vibrational state at 1400 K, and numerous overtones are also excited. Even more excitation is found in CD_4. Because of the large number of vibrational modes excited it is not possible to derive state-specific enhancements from this information.

The reaction mechanism must be quite complicated. At low temperatures the reaction proceeds mainly by bond insertion to form the $[H_3C{-}O{-}O{-}H]^+$ complex. Breaking one of the C−H bonds leads to the major low-energy product, $CH_2O_2H^+$. Breaking the O−O bond yields CH_3O^+, a minor product. Formation of CH_3^+ is approximately thermoneutral and occurs if the C−O bond is broken. The CH_4^+, of course, results from endothermic charge transfer. The other product channels must involve more rearrangement. H_2O^+ can be formed by a hydrogen migration from CH_3 to OH, a migration over 2 heavy atoms. A further migration would be needed to form either HCO^+ or H_3O^+; it is surprising that even though formation of these two products involves substantially more rearrangement than the H_2O^+ channel, they are favored by a large factor. The fact that vibrational energy enhances only these channels may indicate that a different reaction mechanism applies to them and points to the need for detailed dynamical calculations to sort out the reactivity.

Conclusions

The newly acquired ability to study branching ratios at high temperature has been exploited to study the reactions of O_2^+ with CH_4 and CD_4. The data clearly demonstrate the need for high-temperature measurements under truly thermal conditions. We find at 1400 K seven product channels, several not previously observed. Two of the channels, formation of H_3O^+ and HCO^+, involve making and breaking four chemical bonds, the original reason for the in-depth study of this reaction. These two channels comprise 43% of the reactivity at 1400 K. Previously it has been shown that the overall rate for this well-studied reaction is affected by vibrational excitation in CH_4. Comparing the present data to previous beam data shows that CH_4 vibrations enhance the channels that involve extensive bond rearrangement. The present results clearly show that extrapolating other types of experimental kinetics data could not be used to predict the true high-temperature behavior. However, the combination of drift tube and beam data with the true temperature data can lead to important conclusions on how different types of energy affect reactivity.

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