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Rate constants and branching fractions were measured for the reaction of $O^+(^4S)$ with CO_2 as a function of average ion-neutral center-of-mass kinetic energy ($\langle KE_{cm} \rangle$) at several temperatures. The reaction produces both O_2^+ and CO_2^+ as product ions. The total rate constants were found to be nearly collisional at low $\langle KE_{cm} \rangle$ and to decrease slightly at higher $\langle KE_{cm} \rangle$. No temperature dependence of the rate constants was found at any given $\langle KE_{cm} \rangle$, indicating that neither CO_2 rotational excitation nor CO_2 bending mode excitation has much effect on the overall reactivity. In contrast, the branching fraction for the endothermic charge transfer channel leading to CO_2^+ was found to increase with increasing $\langle KE_{cm} \rangle$ and also to increase with temperature at fixed $\langle KE_{cm} \rangle$. Analysis of the data indicates that the branching fraction depends on the total energy in the system (electronic, kinetic, rotational, and vibrational).

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Temperature, kinetic energy, and internal energy dependences of the rate constant and branching fraction for the reaction of O^+ (^4S) with CO_2

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Rate constants and branching fractions were measured for the reaction of O^+ (^4S) with CO_2 as a function of average ion-neutral center-of-mass kinetic energy ($\langle KE_{cm} \rangle$) at several temperatures. The reaction produces both O_2^+ and CO_2^+ as product ions. The total rate constants were found to be nearly collisional at low $\langle KE_{cm} \rangle$ and to decrease slightly at higher $\langle KE_{cm} \rangle$. No temperature dependence of the rate constants was found at any given $\langle KE_{cm} \rangle$, indicating that neither CO_2 rotational excitation nor CO_2 bending mode excitation has much effect on the overall reactivity. In contrast, the branching fraction for the endothermic charge transfer channel leading to CO_2^+ was found to increase with increasing $\langle KE_{cm} \rangle$ and also to increase with temperature at fixed $\langle KE_{cm} \rangle$. Analysis of the data indicates that the branching fraction depends on the total energy in the system (electronic, kinetic, rotational, and vibrational).

I. INTRODUCTION

The reaction of O^+ (^4S) with CO_2 is important in CO_2 release experiments in the earth's ionosphere and is important in the atmospheres of Venus and Mars.[1] The reaction has been extensively studied[1-17] and found to proceed by two channels at low energies,

$$O^+(^4S) + CO_2 \rightarrow O_2^+ + CO + 1.19\ \text{eV} \tag{1a}$$

$$\rightarrow CO_2^+ + O - 0.155\ \text{eV}. \tag{1b}$$

The reaction is efficient. At low energies and temperatures the reaction of O^+ (^4S) is known to produce exclusively O_2^+, a process which is exothermic by more than an electron volt.[18] The charge transfer channel is endothermic[18] and is observed only at elevated temperatures and/or kinetic energies.[1,16] Electronically excited O^+ (^2D,^2P) is known to react with CO_2 to produce CO_2^+ almost exclusively.[13] Thus, various forms of energy promote the endothermic charge transfer channel at the expense of the channel producing $O_2^+ + CO$. The purpose of this paper is to examine the influence of rotations and bending mode vibrations in CO_2 on the reaction of O^+ (^4S) with CO_2. We were particularly interested in whether these forms of energy also promote the charge transfer channel.

II. EXPERIMENT

The measurements were made using the Phillips Laboratory (formerly the Geophysics Laboratory) variable temperature-selected ion flow drift tube apparatus.[19] Instruments of this type have been the subject of review,[20] and only those aspects important to the present study will be discussed in detail.

O^+ was formed from CO by dissociative ionization with electrons in a moderate pressure ion source (~0.1 Torr). This source produced 98% of the O^+ ions in the ground ^4S state. The fraction of excited state O^+ was monitored by allowing the O^+ ions to react with CO in the flow tube. CO charge transfers with the excited metastable states of O^+ (^2D, ^2P) and does not react with the ground state.[21] Therefore, the fraction of O^+ reactant ions which form CO^+ upon CO addition to the flow tube is the fraction of O^+ reactants in excited electronic states. CO_2 and O_2 were tested as alternative sources of O^+ but produced larger fractional amounts of metastable O^+ ions. The 2% fraction of O^+ in the excited state remained approximately constant over the course of these experiments and was examined periodically to check for drift. This small fraction of excited states does not affect the measured rate constants but does affect the determination of the branching fractions.

We were interested in the reaction of O^+ (^4S). Measuring the fraction of O^+ (^2D, ^2P) allowed us to correct for the presence of the excited states. The fraction of excited state O^+ ions could be measured to within ± 25%. The branching fraction for formation of CO_2^+ from the reaction of O^+ (^4S) was determined by subtracting from the total CO_2^+ signal the portion of the CO_2^+ signal due to reaction of the excited state. Since the excited state O^+ ions represented about 2% of the total O^+, this correction added a fixed error of 0.5% (25% of 2%) to the branching fraction for the O^+ (^4S) reaction. We estimate the random error to be 5% of the value of the branching fraction. The total uncertainty in the branching fraction is the square root of the sum of the squares of these independent errors.

Rate constants were measured in the usual manner.[19,20] The precision of the rate constants is estimated to be ± 10% and the accuracy ± 25%. No correction to the rate constants due to the excited states was needed since the rate constants for reaction of the ground and excited states are

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known to be the same,[13] and almost all of the decay was due to reaction of the ground state ion.

The average kinetic energy in the ion-neutral center-of-mass system, $\langle KE_{cm} \rangle$, in the drift tube is derived from the Wannier formula[22] as

$$\langle KE_{cm} \rangle = \frac{(m_i + m_b) m_n}{2(m_i + m_n)} v_d^2 + \frac{3}{2} kT, \tag{2}$$

where m_i, m_b, and m_n are the masses of the reactant ion, buffer gas, and reactant neutral, respectively; v_d is the ion drift velocity; and T is the temperature. The first term in the formula is the energy supplied by the drift field, and the second term is the thermal energy. This formula is an excellent approximation of the relative kinetic energy at low ion energies.[23,24] The CO_2 internal temperature under the conditions of the present experiments is the same as that of the helium buffer gas.

It has recently been shown in our laboratory that dependences of rate constants or branching fractions on the internal temperature of the reactant neutrals can be derived for a variety of ion–molecule reactions by measuring rate constants or branching fractions as a function of $\langle KE_{cm} \rangle$ at several temperatures.[19,24–32] If the reactant ions are monatomic, as in the present study, comparing the rate constants or branching fractions at a particular $\langle KE_{cm} \rangle$ but at different temperatures yields the dependence of the rate constant or branching fraction on the internal temperature of the reactant neutral.

III. RESULTS AND DISCUSSION

The measured rate constants for the overall reaction of O^+ (^4S) with CO_2 are shown in Fig. 1 as a function of $\langle KE_{cm} \rangle$. Below approximately 0.08 eV, the rate constant was found to be approximately 1×10^{-9} cm^3 s^{-1}, independent of $\langle KE_{cm} \rangle$ or temperature within experimental error. Above 0.08 eV, the rate constant was found to decrease. Also shown in Fig. 1 are results from previous room temperature drift tube measurements of this rate constant taken at the University of Birmingham[1] and the University of Pittsburgh.[9] The agreement at low energies is very good, the differences being within less than 10%. At higher energies the Birmingham rate constants are larger than the present results by about 30%, while the Pittsburgh results are larger by about 20%. The three sets of data agree within the combined experimental uncertainties. Agreement with other measurements of thermal rate constants for this reaction is also good.[33]

The values of the overall rate constant measured at different temperatures but similar center-of-mass kinetic energies, $\langle KE_{cm} \rangle$, in Fig. 1 are approximately the same. This indicates that the overall rate constant does not depend on the internal temperature of CO_2. The insensitivity of the rate constant to the internal temperature of CO_2 is expected because reaction occurs on almost every collision. At the temperatures used in this study, both rotations and the bending mode vibration of CO_2 are substantially excited.[34]

Figure 2 shows a plot of the fraction of CO_2^+ produced in the reaction of O^+ (^4S) with CO_2 as a function of $\langle KE_{cm} \rangle$. At all temperatures the branching fraction for the CO_2^+ channel increases with increasing $\langle KE_{cm} \rangle$. The charge transfer channel is slightly endothermic (0.155 eV),[18] and the increase is presumably a consequence of the addition of enough energy to overcome the endothermicity. Two other sets of data are also shown in Fig. 2. Drift tube data taken at the University of Birmingham[1] are shown as a solid line, and beam data obtained at the University of Iowa[16] are shown as a dashed line. The results agree within experimental uncertainty throughout the entire energy range except for the present 545 K results, which, over much of the energy range appear to be significantly higher than either the Birmingham data or our data at similar $\langle KE_{cm} \rangle$

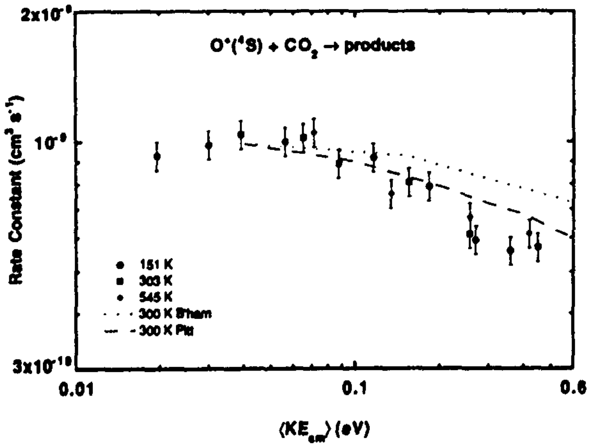

FIG. 1. Rate constants for the reaction of O^+ (^4S) with CO_2 as a function of $\langle KE_{cm} \rangle$. Data obtained at 151, 303, and 545 K are represented by solid circles, squares, and diamonds, respectively. Previous data taken at the University of Birmingham (Ref. 1) and the University of Pittsburgh (Ref. 9) are shown as small dashed and large dashed lines, respectively.

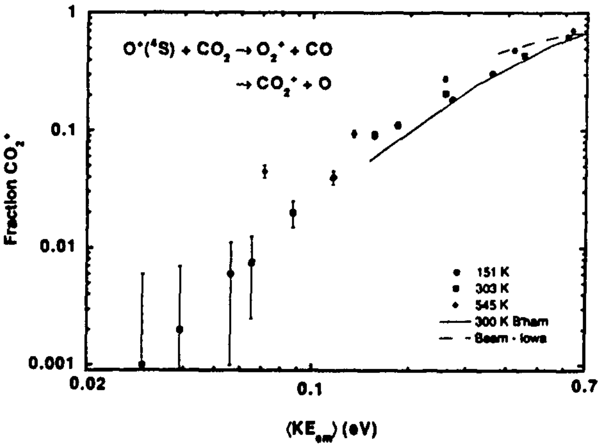

FIG. 2. Branching fractions into CO_2^+ for the reaction of O^+ (^4S) with CO_2 as a function of $\langle KE_{cm} \rangle$. Data obtained at 151, 303, and 545 K are represented by solid circles, squares, and diamonds, respectively. Previous data taken at the University of Birmingham (Ref. 1) and the University of Iowa (Ref. 16) are shown as small dashed and large dashed lines, respectively, where we have simply connected the reported data points with straight lines.

but at lower temperatures. Thus at a particular $\langle KE_{cm} \rangle$, increasing temperature increases the efficiency of the charge transfer channel relative to the atom transfer channel (formation of O_2^+). We attribute the observed differences in branching fractions to differences in the extent of excitation of internal degrees of freedom in CO_2.

Product ion energy distributions taken in a beam apparatus indicate that the reaction between O^+ and CO_2 proceeds through a complex at energies less than 0.8 eV.[17] If the complex lives long enough one may expect that the total energy of the reactants, rather than the initial center-of-mass kinetic energy of the reactants, would control the branching into the two channels. Figure 3 shows the branching fraction of CO_2^+ as a function of average total energy of the reactants. Average total energy is defined as the translational kinetic energy, $\langle KE_{cm} \rangle$, plus the energy stored in the internal degrees of freedom of the CO_2. The CO_2 rotational energy is given by RT, while the energy in vibrations can be evaluated from the product of the vibrational energy and the population in that vibrational energy level summed over all vibrations, i.e., $\Sigma_n\ h\nu_n^*\ \mathrm{pop}(n)$, where $\mathrm{pop}(n)$ is the population of the vibrational state, and ν_n are the vibrational frequencies. The vibrational frequencies are taken from Rothman.[35] This expression for average total energy ignores zero point energy, which would shift the scale by a fixed amount. In Fig. 3 we see that, by plotting the branching fraction versus average total energy, all of the data, including the values measured at 545 K, can be described by a single smooth curve within experimental uncertainty. We note that although the higher energy data are clearly described best by total energy as compared with kinetic energy, it is not clear that the low energy data are as well. Because of large uncertainty at low CO_2^+ fractions due to the presence of excited states of O^+, we are not able to determine the best fit to these data with the same sensitivity as the high energy data. Within the uncertainty of these data, the CO_2^+ branching fraction is described well by the average total energy. Above a branching fraction of 0.01–0.02, where the error due to the excited states of O^+ is small, the temperature data agree remarkably well, i.e., the branching fraction at a particular $\langle KE_{cm} \rangle$ appears to be temperature independent. The ability to describe all the branching fraction data with a single curve indicates that total energy is the principal factor in determining the branching fraction. This conclusion is supported further by our previous results[13] showing that electronically excited O^+ reacts to form CO_2^+ almost exclusively.

Despite the facts that the charge transfer channel dominates the reaction when it is energetically possible, that kinetic energy and internal energy (as described by the total energy) appear to be equally efficient in promoting the charge transfer channel, and that the overall reaction is very efficient (~90% of the collisions result in reaction at low energy), the charge transfer channel is nevertheless relatively inefficient, as shown below.

The rate constant for charge transfer is the product of the branching fraction and the rate constant for the overall reaction. The maximum value of the charge transfer rate constant at a given temperature is given by the collision rate constant multiplied by a Boltzmann factor. We can estimate this maximum rate constant by using the Langevin rate constant of $1.17\times10^{-9}\ \mathrm{cm^3\ s^{-1}}$ for the collision rate constant and a pseudo Boltzmann factor given by $\exp\{-0.155\ \mathrm{eV}/([2/3]^*\langle\text{total energy}\rangle)\}$. We chose to use the average total energy in the Boltzmann factor because our data indicate that all forms of energy promote the charge transfer reaction. Use of $\langle KE_{cm} \rangle$ in the Boltzmann factor yields qualitatively similar results. The maximum rate constants are compared to the measured values in Fig. 4. We find that the efficiency for charge transfer ranges from 5% to 60% over the full energy range of these experiments. Most of the data fall between 20% and 40% efficiency, and the efficiencies

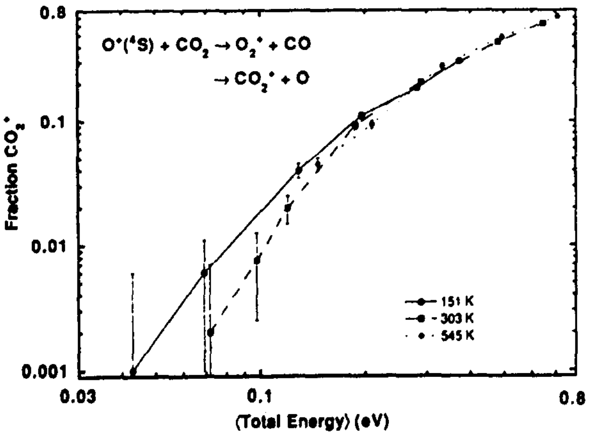

FIG. 3. Branching fractions into CO_2^+ for the reaction of O^+ (^4S) with CO_2 as a function of average total energy. Data obtained at 151, 303, and 545 K are represented by solid circles, squares, and diamonds, respectively. The points at 151, 303, and 545 K are connected by solid, large dashed, and small dashed lines, respectively, for clarity.

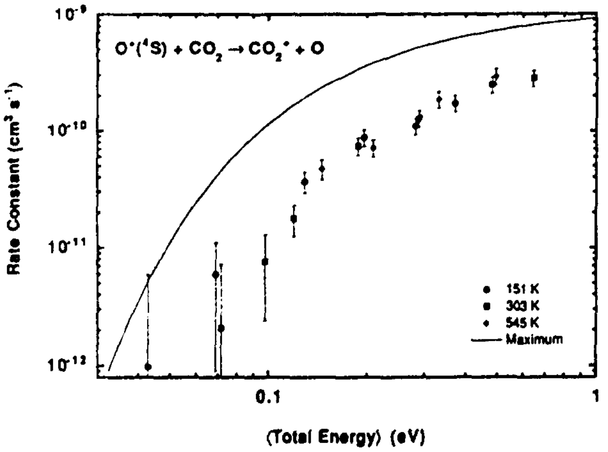

FIG. 4. Charge transfer rate constants as a function of $\langle$total energy$\rangle$. The solid line represents the maximum possible value as described in the text. The points represent the experimental rate constants evaluated from the CO_2^+ branching fraction and overall rate constant data (see text). Data obtained at 151, 303, and 545 K are represented by solid circles, squares, and diamonds, respectively.

increase slowly with increasing energy. At the higher kinetic energies, however, the Langevin collision rate constant is a lower limit to the collision rate constant. Use of the appropriate collision rate constant would therefore reduce the efficiency at the higher energies. For comparison, using a reasonable hard sphere cross section, we estimate that the true collision rate constant at these energies is no more than twice the Langevin value.

The inefficiency of the charge transfer channel is, at least in part, related to the competing channel forming $O_2^+ + CO$ because the overall reaction is approximately 100% efficient (at least at low energies). Both channels of the reaction are believed to proceed through a (possibly common) complex[17] over this energy range. At energies near threshold, statistics would still favor the reactive channel over the charge transfer channel since the relative number of states for the endothermic channel will be small. The slowly increasing efficiency with increasing energy may then be related to the decreasing fraction of energetically allowed collisions that are near threshold energy.

While total energy appears to control the branching fractions in this reaction, the precision of our data only reveals the apparent equivalence of vibrational energy and kinetic energy. Specifically, the 545 K data in Fig. 2 are significantly larger in value than the 303 or 151 K data at a similar $\langle KE_{cm} \rangle$. In Fig. 3 (when plotted versus average total energy) the data appear to be the same at a given total energy. The largest internal energy contribution to the total energy for 545 K is the vibrational energy. At 545 K there is considerably more vibrational excitation in the CO_2 than at 303 K or 151 K. At 545 K, 33% of the CO_2 molecules are vibrationally excited, and 10% have more than 1 quantum of excitation, while at 303 K, 8% of the CO_2 molecules are vibrationally excited (bending mode),[35] and only 0.6% have more than 1 quantum of excitation.

Rotational energy effects would be most apparent at low temperatures and energies, but our data do not reveal such an effect. The branching fractions measured at 303 and 151 K at similar $\langle KE_{cm} \rangle$ are approximately the same. Although the lack of temperature dependence in this range could be interpreted as a lack of rotational energy dependence, we feel that a more likely explanation is that rotational energy behaves like other forms of energy, but our data are not precise enough to measure these differences. At low energies, where the effect is expected to be largest, the large errors due to the presence of excited states of O^+ inhibit our ability to see such an effect. At higher energies, if rotational energy were equivalent to all other types of energy, the effect would be too small to measure, i.e., our random error is too large.

We have previously shown evidence that rotational energy can be used to drive an endothermic charge transfer reaction,[24,25] i.e., in the reaction of Ar^+ with N_2. In fact, many aspects of this reaction are similar to those described above for the reaction of O^+ with CO_2. The charge transfer reaction of Ar^+ with N_2 also proceeds through two main channels,

$$Ar^+ (^2P_{3/2}) + N_2 \rightarrow Ar + N_2^+ (v=0) + 0.179 \text{ eV} \quad (3a)$$

$$\rightarrow Ar + N_2^+ (v=1) - 0.092 \text{ eV}. \quad (3b)$$

One of the channels is exothermic and one is endothermic. The rate constant for channel (3a) is small, and above 140 K, the endothermic channel (3b) dominates the reactivity. These results are similar to the present observations in that the endothermic channel dominates once it is energetically accessible. As in the reaction of O^+ with CO_2, reaction (3) is thought to proceed through a complex at low energies.[11,36] We have found that the overall rate constant at 300 K and above increases with increasing temperature of the N_2 neutral and also with increasing $\langle KE_{cm} \rangle$.[25] However, when the rate constant is plotted as a function of average total energy of the reactants, the data can be described by a single smooth curve. In the reaction of Ar^+ with N_2, no appreciable vibrational excitation of the N_2 reactant occurred at the temperatures of the study. Therefore the data indicate that kinetic energy and rotational energy are equally effective in driving the endothermic reaction (3b). Thus, as found also in the present study, the efficiency of the endothermic reaction is principally determined by the average total energy. The equivalence of rotational energy and kinetic energy in the reaction of Ar^+ with N_2 lends support to the interpretation that rotational energy is equivalent to other forms of energy for the purpose of driving the endothermic charge transfer reaction of O^+ with CO_2.

In summary, all types of energy seem to be equally effective in promoting the endothermic charge transfer between O^+ and CO_2. Previous measurements have shown that both kinetic and electronic energy in O^+ increase the probability of the charge transfer channel. The present results indicate that CO_2 bending mode energy and possibly also CO_2 rotational energy increase the probability of the charge transfer channel as well. The equivalence of all types of energy probably results from energy pooling in a long lived complex. This conclusion is in agreement with the results for the reaction of Ar^+ with N_2. Finally, although all types of energy promote the charge transfer reaction, this reaction channel does not always proceed whenever it is energetically accessible, i.e, it is inefficient. We suggest that the cause of this inefficiency could be revealed in a theoretical investigation of this reaction.

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