Rate coefficients for the endothermic reactions $C^+(^2P) + H_2(D_2) \rightarrow CH^+(CD^+) + H(D)$ as functions of temperature from 400–1300 K

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We have measured the bimolecular rate coefficients for the reactions of $C^+(^2P)$ with H_2 and D_2 as functions of temperature from 400 to 1300 K using a high temperature flowing afterglow apparatus. The temperature dependences of these rate coefficients are accurately fit by the Arrhenius equation, with activation energies equal within experimental uncertainty to the reaction endothermicities. Internal energy dependences have been deduced by combining the present data with previous drift tube and ion beam measurements. We found that reactant rotational energy and translational energy are equally effective in surmounting the energy barrier to reaction, and that vibrational excitation of the neutral reactant to the $v=1$ state enhances the rate coefficients by a factor of ~ 1000 for the reaction with H_2 and by ~ 6000 for the reaction with D_2 at temperatures of 800 and 500 K, respectively. This vibrational enhancement is larger than the enhancement that would be produced if the same amount of energy were put into translational and/or rotational modes of the reactants. In addition, rate coefficients have been derived for the three-body association reaction of $C^+(^2P)$ with H_2 in a helium buffer over the temperature range 300–600 K. © 1997 American Institute of Physics. [S0021-9606(97)01724-8]

INTRODUCTION

Over the past two decades, considerable attention has been given to the gas-phase ion–molecule reaction

$$\Delta H_0^\circ = 0.398 \pm 0.003 \text{ eV},$$

and its deuterium analog

$$\Delta H_0^\circ = 0.430 \pm 0.005 \text{ eV}.$$

There are several reasons for the continuing interest in the $C^+ + H_2$ reaction. First, it has become a model system for experimental and theoretical studies of the kinetics, dynamics, and energy requirements of endothermic ion–molecule reactions. Second, it is one of the simplest triatomic, three-electron systems involving a p electron, and the system has several potential energy surfaces. Third, experimental data on this reaction can be used as a benchmark against which theoretical treatments of ion–molecule reactions can be tested. Fourth, the reaction is of astrophysical significance as a possible source of the CH^+ ions observed in interstellar clouds.^{1–8}

Consequently, this system has been the subject of numerous theoretical studies, including *ab initio* potential energy surface computations,^{9–14} classical trajectory studies,^{15,16} and phase space^{17–21} and transition state²² theory calculations.

Equally numerous are the experimental studies, which to date have relied upon various ion acceleration techniques to overcome the reaction endothermicity. Ion beam methods have been used to determine integral reaction cross sections,^{23–26} product velocity vector distributions,^{27–29} and rotational-vibrational state distributions of electronically excited products^{30–32} as functions of the relative translational energy of the reactants. Additionally, selected ion flow drift tubes have been used^{33,34} to measure rate coefficients as functions of translational energy.

In spite of the considerable attention these reactions have received, there have been no reported measurements of the rate coefficients under conditions of thermal equilibrium. In this paper, we present the first such measurements, made over the temperature range 400–1300 K using our newly constructed high temperature flowing afterglow (HTFA) apparatus. We compare these thermal rate coefficients with the phenomenological rate coefficients obtained from the previous ion beam and drift-tube studies, thereby elucidating the effect of the internal energy of the neutral reactant upon the rate coefficient.

Additionally, we report here rate coefficients from 300–600 K for the three-body association reaction

which is exothermic by 4.34 eV (Ref. 35) for formation of the product ion in its $CH_2^+(^2A_1)$ ground electronic state and, at the He buffer gas concentrations used in this study, competes effectively with the endothermic two-body channel [reaction (1)] below ~ 600 K. The rate coefficients determined in the present study are compared with those measured pre-

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viously over the temperature range 80–300 K by other workers utilizing flowing afterglow,³⁶ drift tube,³⁷ and selected ion flow tube³⁸ techniques.

A third possible reaction channel, radiative association,

has been studied at low temperatures (10–80 K) using ion trap techniques,^{39,40} which have yielded rate coefficients for radiative association, k_r , on the order of $10^{-15} \text{ cm}^3 \text{ s}^{-1}$ at these temperatures. Theoretical calculations of k_r have also been performed;^{41,42} the results obtained are in reasonable accord with the measured values and predict a marked decrease in k_r with increasing temperature above 100 K. Consequently, reaction (4) will not compete with reactions (1) and (3) at the elevated temperatures of the present study.

EXPERIMENT

The experiments reported here were carried out using the Phillips Laboratory high temperature flowing afterglow (HTFA) apparatus. This instrument has been described in detail recently,⁴³ so just a brief description is given here. Reactant ions are produced by electron impact in the upstream, water-cooled section of a ceramic flow tube. A helium buffer carries the ions downstream, where the flow tube is heated by a commercial furnace. After the ions have reached thermal equilibrium, the neutral reactant gas is added midway down the flow tube. At the end of the flow tube, a small fraction of the gas mixture is sampled, and the remainder is pumped by a Roots blower. The ions in the gas sample are analyzed by a quadrupole mass filter and detected by an electron multiplier using pulse counting techniques. The decay of the primary ion signal as a function of the neutral reactant gas concentration yields the effective two-body rate coefficient, k_{eff} .

The C^+ reactant ions were produced from research grade CO, which was introduced into the instrument without further purification. Dissociative ionization of the CO was presumably caused both directly by electron impact and indirectly by Penning ionization from metastable He atoms. The nominal electron energy was kept below 25 eV to ensure that only $C^+(^2P)$ ground state ions were produced. [The appearance energy for forming $C^+(^2P) + O^-$ from CO is ~ 21 eV (Ref. 44) and the first electronically excited state of the carbon ion, $C^+(^4P)$, lies 5.4 eV above the ground state.⁴⁵] Sufficient CO was added to ensure that production of C^+ by Penning ionization was complete before the neutral reactant inlet.

Spin-orbit coupling splits the ground state of the carbon ion into two states, the $C^+(^2P_{1/2})$ and the $C^+(^2P_{3/2})$, which are separated by 8 meV.⁴⁵ These are probably both produced in the ion source region, presumably in the ratio of their statistical weights. Calculated rate coefficients⁴⁶ indicate that the excitation ($^2P_{1/2} \rightarrow ^2P_{3/2}$) of C^+ ions by helium is fast ($k \sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) at the high temperatures of this study. This, combined with the frequent C^+ –He collisions, will maintain a constant ratio of the two spin-orbit states of C^+ along the flow tube, thereby making it impossible to derive

FIG. 1. Decay plots for the reactions of C^+ with H_2 in He buffer at temperatures of 400, 700, and 1000 K.

any information on the relative rate coefficients of the two spin-orbit states from the present measurements.³⁴

The helium buffer gas and the neutral reactant gases were each passed through liquid nitrogen cooled traps to reduce the concentration of water vapor and other possible impurities. No attempt was made to measure the CH^+ (or CD^+) product ions because it is known from previous work⁴⁷ that CH^+ is rapidly ($k \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) converted to CH_2^+ and then to CH_3^+ via secondary reactions with excess H_2 .

We estimate the error in the rate coefficient reported here as $\pm 25\%$ and $\pm 15\%$ for the total and the relative error, respectively.

RESULTS

Figure 1 shows a semilog plot of the reactant ion count rate versus reactant neutral concentration for the reaction of C^+ with H_2 at several temperatures. The plots show good linearity, indicating that source conditions are such that no detectable amounts of C^+ in electronically excited states are present and that production of C^+ is complete by the time the neutral reactant is added. Effective two-body rate coefficients k_{eff} for the consumption of C^+ are derived from the slopes of these lines and a knowledge of the ion flight time.

Since the C^+ ion is consumed by both the bimolecular atom-transfer reaction (1) and the termolecular association reaction (3), the effective two-body rate coefficient k_{eff} measured for the decay of the C^+ signal with added H_2 is given by the equation

$$k_{\text{eff}} = k_2 + k_3[\text{He}], \quad (5)$$

where k_2 is the rate coefficient for the bimolecular atom-transfer reaction (1), k_3 is the rate coefficient for the termolecular association reaction (3), and $[\text{He}]$ is the helium con-

FIG. 2. Effective two-body rate coefficients for the reactions of C^+ with H_2 in He buffer at 400 K versus He concentration. Error bars of $\pm 15\%$ represent the reproducibility of the rate constant. The straight line represents the linear regression fit to the data.

centration. Figure 2 shows a plot of the effective two-body rate coefficients measured for the reaction of C^+ with H_2 at 400 K at varying buffer gas concentrations versus $[He]$. The straight line represents a linear regression fit of Eq. (5) to the data, from which the rate coefficients k_2 and k_3 are determined at this temperature.

For the reaction of C^+ with H_2 , k_2 and k_3 were determined by this process over the temperature range 300–600 K. The termolecular rate coefficients k_3 determined from plots of k_{eff} vs $[He]$ from 300–600 K are plotted versus temperature in Fig. 3. The flattening out of our results at the higher temperatures is probably an artifact caused by the difficulty in accurately determining the slope of k_{eff} vs $[He]$ when $k_2 \gg k_3[He]$, as becomes the case at the higher temperatures. Nevertheless, the present results are in reasonable

FIG. 3. Termolecular rate coefficients versus temperature for the reaction $C^+ + H_2 + He \rightarrow CH_2^+ + He$. The circles represent the results obtained in the present HTFA study. The triangle is from Fheseinfeld *et al.* (Ref. 36), the square from Johnsen *et al.* (Ref. 37), and the diamonds from Adams and Smith (Ref. 38). The solid line represents an empirical fit to the latter's data (see text).

FIG. 4. Bimolecular rate coefficients versus temperature for the reaction $C^+ + H_2 \rightarrow CH^+ + H$. The solid circles are the results obtained in the present HTFA study from 400 to 1300 K; error bars are assigned as discussed in the text. The dotted line represents the analytical expression [Eq. (6) in text] of Solomon and Klemperer (Ref. 48), the dashed line represents the expression [Eq. (7) in text] derived by Herbst and Knudsen (Ref. 19), and the solid line represents the results [Eqs. (8) and (9) in text] of phase space calculations by Gerlich *et al.* (Ref. 21).

agreement with previous measurements of k_3 over the temperature range 80–300 K by Fehsenfeld *et al.*,³⁶ Johnsen *et al.*,³⁷ and Adams and Smith.³⁸ An empirical fit to the latter's data gives the temperature dependence of the termolecular rate coefficient for the association of C^+ with H_2 in the presence of He as $k_3 = 2.5 \times 10^{-26} T^{-1.41} \text{ cm}^6 \text{ s}^{-1}$.

At temperatures greater than 600 K, k_2 had increased to such an extent that the termolecular association reaction made only a minor ($< 5\%$) contribution to the consumption of C^+ . At these higher temperatures, the empirical expression given above for k_3 was used to deduce the value of k_2 from the measured value of k_{eff} . Figure 4 shows the temperature dependence of the bimolecular rate coefficient, k_2 , for reaction (1) derived as described in this and the preceding paragraphs from the measured value of k' over the range 400–1300 K. The error bars assigned to k_2 from 400–600 K represent one standard deviation in the intercept found from the linear regression analysis of the k_{eff} vs $[He]$ data at each temperature in this range; at temperatures above 600 K, the error bars shown are based on a propagation of errors, with uncertainties of $\pm 25\%$ assigned to both the measured value of k_{eff} and the calculated value of k_3 .

For the reaction of C^+ with D_2 , no attempt was made to derive the termolecular rate coefficient experimentally because of the large amounts of D_2 that would have been required. Instead, the temperature dependence of k_3 was deduced from an empirical fit to the data of Adams and Smith³⁸ on the termolecular association of C^+ with D_2 in a helium buffer over the temperature range 87–287 K. The expression obtained, $k_3 = 2.2 \times 10^{-26} T^{-1.25} \text{ cm}^6 \text{ s}^{-1}$, was then used to derive the bimolecular rate coefficient, k_2 , for reaction (2) from the measured value of the effective two-body rate coefficient, k_{eff} , and the calculated value of k_3 at each temperature. Figure 5 shows the bimolecular rate coefficient, k_2 ,

FIG. 5. Bimolecular rate coefficients versus temperature for the reaction $C^+ + D_2 \rightarrow CD^+ + D$. The solid circles are the results obtained in the present HTFA study from 500 to 1300 K; error bars are assigned as discussed in the text.

obtained in this manner for reaction (2) as a function of temperature over the range 400–1300 K. The error bars shown are based on a propagation of errors, with uncertainties of $\pm 25\%$ assigned to both the measured value of k_{eff} and the calculated value of k_3 .

DISCUSSION

In the absence of previous experimental measurements of the thermal rate coefficients for the reaction of C^+ with H_2 , several analytical expressions have been proposed over the years for the temperature dependence of the bimolecular rate coefficient for this reaction. In 1972, Solomon and Klemperer⁴⁸ used the beam data of Maier²³ to derive the formula

$$k_2 = (7.5 \times 10^{-15}) \cdot T^{5/4} \cdot \exp(-4700/T) \text{ cm}^3 \text{ s}^{-1}. \quad (6)$$

This formula served as the accepted analytical expression for k_2 until the 1980s, when several other workers^{18b,19,21} derived expressions predicting significantly larger values for k_2 . As can be seen in Fig. 4, the rate coefficients calculated from Eq. (6) (shown as the dotted line labeled SK) are 10–50 times smaller than the measured values obtained in the present HTFA study.

In 1981, Herbst and Knudsen¹⁹ proposed the expression

$$k_2 = (3.5 \times 10^{-10}) \exp(-4550/T) \text{ cm}^3 \text{ s}^{-1}, \quad (7)$$

as a fit to the results of their nonequilibrium phase space calculations for the reaction of C^+ with H_2 . Rate coefficients calculated from this equation (shown as the dash-dotted line labeled HK in Fig. 4) are roughly a factor of 2–3 smaller than the measured values of k_2 obtained in the present study over the temperature range 400–1300 K.

In the mid-1980s, utilization of the guided ion beam (GIB) technique yielded significantly more accurate data than had previously been available on the excitation function (i.e., translational energy dependence of the integral cross section) for the reaction of C^+ with H_2 . Ervin and

Armentrout²⁶ derived an empirical expression for the true (i.e., unconvoluted) excitation function from their experimental data by fitting their measured cross sections with effective cross sections calculated by convoluting a trial function containing adjustable parameters with their experimental energy distributions. By integrating this empirical expression over a Boltzmann energy distribution, they then computed a value of $1.2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for the thermal rate coefficient at 300 K, a value which agrees well with an extrapolation of the present HTFA data to room temperature.

Phase space theory (PST) has been used^{18b,20} to model the results of this GIB study. Ervin and Armentrout²⁰ found that PST accurately reproduced both the magnitude and the translational energy dependence of their measured cross sections. By averaging their theoretically calculated cross sections over a Boltzmann energy distribution, they computed a value of $1.0 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ for the thermal rate coefficient for reaction (1) at 300 K, a value which agrees well with their experimentally determined value at that temperature.

The excitation function for reaction (1) was measured in a second GIB study by Gerlich *et al.*,²¹ who obtained excellent agreement with the results reported by Ervin and Armentrout.²⁶ In addition, by using different ortho-para mixtures of H_2 , Gerlich *et al.*²¹ obtained information on the dependence of the cross section upon reactant rotational energy, and used PST to derive state-specific cross sections. Thermal rate coefficients for individual rotational states, $k(T;J)$, were then calculated by numerical integration of the properly weighted cross sections. They found that these state-specific rate coefficients for reaction (1) could be well approximated for $J \leq 7$ by an Arrhenius equation of the form

$$k_2(T;J) = (1.58 \times 10^{-10}) \cdot \exp\{-[\Delta H_0^\circ - E(J) + 0.018 \text{ eV}]/kT\}, \quad (8)$$

where $k_2(T;J)$ has units of $\text{cm}^3 \text{ s}^{-1}$, $\Delta H_0^\circ = 0.398 \text{ eV}$, $E(J)$ is the rotational energy of the hydrogen molecule in eV, k is Boltzmann's constant, and T is in Kelvin. The difference of 0.018 eV between the Arrhenius activation energy and the effective threshold energy $\Delta H_0^\circ - E(J)$ is an empirically determined parameter introduced by Gerlich *et al.*²¹ to optimize the fit of their measured cross sections in the threshold region with their assumed excitation function.

In order to compare these PST predictions with our present measurements, we have calculated thermal rate coefficients at a number of temperatures over the range 400–1300 K from the equation

$$k_2(T) = \sum p(J;T) \cdot k_2(T;J), \quad (9)$$

where $k_2(T)$ is the bimolecular rate coefficient predicted by PST at temperature T , and $p(J;T)$ is the population of rotational state J in normal hydrogen at temperature T . For $J \leq 7$ (i.e., for $E(J) < \Delta H_0^\circ + 0.018 \text{ eV}$), $k_2(T;J)$ is calculated from Eq. (8) using the values of $E(J)$ given in Ref. 21. For $J > 7$, it is assumed that $k_2(T;J) = 1.58 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The results of this thermal averaging, shown as the solid line labeled GSD in Fig. 4, agree remarkably well with

FIG. 6. Arrhenius plot of the data shown in Fig. 4 for the reaction $C^+ + H_2 \rightarrow CH^+ + H$. The straight line represents the linear regression fit to the data.

our measured rate coefficients over most of the temperature range of this study. This agreement is a necessary (but not a sufficient) proof of the efficacy of reactant rotational energy in surmounting the energy barrier to reaction as explicitly stated in Eq. (9).

An Arrhenius plot of the measured rate coefficients for reaction (1) is shown in Fig. 6. The straight line represents a linear regression fit of the equation $k(T) = A \exp(-E_a/RT)$ to the HTFA data. As can be seen, the data show excellent agreement (coefficient of determination, $R^2 = 0.9997$) with the Arrhenius equation over the entire temperature range studied. The Arrhenius parameters obtained from this fit are $A = (7.4 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $E_a = 0.391 \pm 0.005 \text{ eV}$, with the quoted uncertainties representing one standard deviation. The value of the activation energy, E_a , is equal within experimental uncertainty to the reaction endothermicity, $\Delta H_0^\circ = 0.398 \pm 0.003 \text{ eV}$, indicating that there is no energy barrier to the reaction other than its endothermicity, a finding in agreement with the crossed beam, high resolution threshold determination by Gerlich *et al.*²¹ The value of the frequency factor, A , is about 0.46 of the collision rate coefficient ($1.62 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) calculated from the simple Langevin model,⁴⁹ which approximates the interaction potential by that of a charge-induced dipole, using the value of $0.819 \times 10^{-24} \text{ cm}^3$ for the polarizability of H_2 .⁵⁰ This result is consistent with *ab initio* calculations,^{9–12} which show that only two of the six nearly degenerate electronic states available to the reactants can lead to reaction under thermal conditions because of high energy barriers on the other four adiabatic potential surfaces. This would lead to an electronic degeneracy factor of 2/6 if one ignores the spin-orbit splitting and assumes that all six states are equally populated in the entrance channel, although somewhat higher factors are possible under other scenarios.^{19,21}

For the reaction of C^+ with D_2 , an Arrhenius plot (shown in Fig. 7) of the bimolecular rate coefficients yields values of $(8.0 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $0.422 \pm 0.006 \text{ eV}$ for the parameters A and E_a , respectively, with $R^2 = 0.9980$. As was

FIG. 7. Arrhenius plot of the data shown in Fig. 5 for the reaction $C^+ + D_2 \rightarrow CD^+ + D$. The straight line represents the linear regression fit to the data.

the case for reaction (1), the value found for the activation energy, E_a , of reaction (2) is equal within experimental uncertainty to the endothermicity ($0.430 \pm 0.005 \text{ eV}$) of the reaction. The frequency factor, A , is about 0.66 the Langevin collision rate coefficient ($1.22 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$) for the reaction of C^+ with D_2 , a ratio somewhat higher than was found for the reaction of C^+ with H_2 . Given the experimental uncertainties in the determination of the frequency factors for the two reactions and the simplistic nature of the Langevin model for collision rates, it is not clear that any real significance should be ascribed to this disparity in ratios.

The expression for the state-specific rate coefficients for reaction (1) [Eq. (8)] derived by Gerlich *et al.*²¹ as an empirical approximation to their PST calculations, predicts explicitly that rotational excitation of the neutral reactant enhances the rate coefficient for this endothermic reaction by lowering the effective energy barrier to reaction. The finding that thermal rate coefficients calculated from Eq. (7) agree very well with our measured values supports, but does not prove, the validity of this prediction. More direct evidence concerning the effect of reactant internal energy upon reactivity can be obtained by comparing the thermal rate coefficients measured in the present HTFA study with nonthermal rate coefficients measured in drift tube or beam experiments, where the translational energy of the reactants can be varied independently of the internal energy of the neutral reactant, the latter being fixed by the temperature (typically 300 K) of the neutral reactant.

Such a comparison for the reaction of C^+ with H_2 is shown in Fig. 8. Nonthermal rate coefficients measured by Twiddy *et al.*³⁴ in drift tube (DT) study (crosses) and those measured by Erwin and Armentrout^{26b} in a guided ion beam (GIB) experiment (triangles) are plotted versus average total (translational+rotational) energy per molecule. Since the H_2 reactant was at room temperature in the nonthermal experiments, the rotational contribution ($kT = 0.026 \text{ eV}$) to the total energy was generally much smaller than the translational contribution. The rate coefficients measured in these

FIG. 8. Bimolecular rate coefficients obtained in the present HTFA study for the reaction $C^+ + H_2 \rightarrow CH^+ + H$ plotted versus average translational energy, $3kT/2$, (open circles), and versus average total (translational plus rotational) energy, $5kT/2$, (solid circles). Data from a previous drift tube experiment at room temperature by Twiddy *et al.* (Ref. 34) are shown as crosses, and data from a guided ion beam study by Ervin and Armentrout (Ref. 26) are shown as triangles.

two experiments show remarkably good agreement, especially considering the differences in the experimental techniques employed. (The GIB results obtained by Gerlich *et al.*²¹ were essentially indistinguishable from the results of these experiments and thus were not included.) The thermal rate coefficients measured in the present HTFA study are plotted in two ways; first, versus the average translational energy, $3kT/2$, of the reactants (open circles), and second, versus the average total energy, $5kT/2$, of the reactants (solid circles). Comparison of the first representation of the HTFA data (open circles) with the drift tube and beam data is equivalent to comparing reactants possessing nearly equivalent translational energies but quite different internal energies; this comparison clearly shows that the greater internal energy of the H_2 reactant in the HTFA experiment causes approximately a ten-fold increase in the magnitude of the rate coefficient measured at the same translational energy with room temperature H_2 .

When the rotational energy of the H_2 reactant is included (solid circles), the HTFA results show excellent agreement (particularly at the lower end of the temperature range studied) with the drift tube and beam data at the same value of the average *total* energy, despite the fact that the relative proportions of translational and rotational energy are quite different in the HTFA and drift tube/beam experiments. This clearly shows that reactant rotational and translational energy are equally effective in overcoming the endothermicity of this reaction.

The agreement between the HTFA data plotted versus $5kT/2$ and the drift tube/beam data is not as good at the higher end of the temperature range studied as it is at the lower, with the HTFA thermal rate coefficients being 10%–20% greater than the drift tube/beam rate coefficients. This disparity may be an artifact caused by differences in the widths of the energy distributions in the two sets of experi-

FIG. 9. Bimolecular rate coefficients obtained in the present HTFA study for the reaction $C^+ + D_2 \rightarrow CD^+ + D$ plotted versus average translational energy, $3kT/2$, (open circles), and versus average total (translational plus rotational) energy, $5kT/2$, (solid circles). Data from a previous drift tube experiment at room temperature by Twiddy *et al.* (Ref. 34) are shown as crosses, and data from a guided ion beam study by Ervin and Armentrout (Ref. 26) are shown as triangles.

ments at the same average energy, or it might be caused by the onset of a vibrational contribution to the internal energy of H_2 . Due to the high vibrational frequency of H_2 (4400 cm^{-1} , equivalent to a vibrational spacing of 0.545 eV), the population of $H_2(v=1)$ is insignificant at the lower temperatures and has been ignored in this analysis; however, by 1300 K the population of $H_2(v=1)$ has risen to 0.76% . Since the reaction $C^+ + H_2(v=1) \rightarrow CH^+ + H$ is exothermic, this relatively small percentage of vibrationally excited H_2 could measurably enhance the overall rate coefficient.

Figure 9 shows a similar comparison between the HTFA results and the drift tube/beam results for the reaction of C^+ with D_2 . The general features are similar to those discussed above with regard to the reaction of C^+ with H_2 , thus reinforcing the conclusion that reactant rotational and translational energy are equally effective in overcoming the endothermicity of this reaction. This same conclusion has also been reached in four other studies of rotational effects on the rates of endothermic ion molecule reactions⁵¹ and, since no exceptions have yet been found, seems to be quite general.

A second important feature displayed in Fig. 9 is that the discrepancy between the HTFA data plotted versus $5kT/2$ and the drift tube/beam data at the higher temperatures is much more marked for the reaction with D_2 than for the reaction with H_2 . This observation strongly suggests that the greater reactivity found in the HTFA study at a given value of (translational+rotational) energy is caused by vibrational excitation of the D_2 reactant, for which the vibrational frequency is 3111 cm^{-1} (equivalent to a vibrational spacing of 0.385 eV), thereby resulting in $D_2(v=1)$ population of 3.1% at 1300 K .

We have derived the rate coefficients for the reactions of C^+ with vibrationally excited H_2 and D_2 from the two sets of data (HTFA and GIB) for each reaction and from the calcu-

FIG. 10. Bimolecular rate coefficients derived as described in the text for the reactions of C^+ with $H_2(v=1)$ (open circles) and $D_2(v=1)$ (solid circles).

lated H_2 (or D_2) vibrational populations as a function of temperature. The rate coefficient at a given temperature can be written as

$$k_2(T) = \sum p(v;T) \cdot k_2(T;v), \quad (10)$$

where $k_2(T)$ is the measured thermal (i.e., HTFA) rate coefficient as a function of temperature, $k_2(T;v)$ is the rate coefficient at temperature T for a given vibrational state of the neutral reactant, and $p(v;T)$ is the Boltzmann population of that vibrational state at temperature T . Because of the high vibrational frequencies of H_2 and D_2 , the term $p(v;T)$ decreases very rapidly with increasing v at the temperatures of the present study, and only the first two terms ($v=0,1$) of the sum need be considered. We take $k_2(T;v=0)$ as the rate coefficient measured by Ervin and Armentrout^{26b} in a GIB experiment with room-temperature neutral reactant, where the temperature is derived from $E_{c.m.}$ (the center-of-mass translational energy) from the relationship $3kT/2 = E_{c.m.}$, and solve Eq. (10) for $k_2(T;v=1)$. The results are shown in Fig. 10 as $k_2(v=1)$ for the reactions of C^+ with vibrationally excited H_2 (open circles) and D_2 (solid circles). From a propagation of errors treatment, we estimate a factor of 2 uncertainty in the reported values. (This relatively large uncertainty is primarily an artifact caused by using the small differences between the HTFA data and the GIB data to derive the rate coefficients for the vibrationally excited neutral reactants.)

The rate coefficients thus derived for the reaction of C^+ with $H_2(v=1)$ are in the range $1-2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, which is approximately the Langevin collision rate coefficient, and show a slight negative temperature dependence. This reaction is exothermic by 0.147 eV for the formation of $CH^+(v=1)$, and both the magnitude and the temperature dependence of the derived rate coefficients are typical of an exothermic ion-molecule reaction. At 800 K, the lowest temperature for which we could derive a rate coefficient for

this reaction, the ratio $k_2(v=1)/k_2(v=0) \approx 1000$. This ratio diminishes with increasing temperature, falling to a value of about 50 at 1300 K.

The derived rate coefficients for the reaction of C^+ with $D_2(v=1)$ are smaller ($3-5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and show a slight positive temperature dependence, as would be expected for this reaction, which is endothermic by 0.047 eV for the formation of $CD^+(v=1)$. The vibrational enhancement is even more striking in this case than for the reaction with H_2 . At 500 K, the ratio $k_2(v=1)/k_2(v=0) \approx 6000$, the largest vibrational effect upon reactivity that we have observed. Again, this ratio diminishes with increasing temperature, falling to a value of about 20 at 1300 K.

Comparison of the $k_2(v=1)$ results with the $d_2(v=0)$ data from the DT/GIB experiments shows that vibrational excitation of the neutral reactant produces a greater enhancement of the rate coefficient than would occur from increasing the translational and/or rotational energy of the reactants in their ground vibrational state by the same amount. We have observed similar behavior in other systems.⁵¹

SUMMARY

A high temperature flowing afterglow apparatus has been used to measure for the first time the thermal rate coefficients for the endothermic ion-molecule reactions $C^+(^2P) + H_2(D_2) \rightarrow CH^+(CD^+) + H(D)$. The wide temperature range studied, 400–1300 K, allows detailed comparison of the results obtained with theoretical models for this reaction and with microscopic rate coefficients measured as functions of reactant translational energy in drift tube and ion beam experiments.

The Arrhenius equation has been found to provide an accurate empirical fit to the temperature dependence of the rate coefficients for these reactions, with the activation energies equal to the reaction endothermicities and the frequency factors being about 1/3–2/3 of the Langevin collision rate constant.

The results obtained for the reaction of $C^+(^2P)$ with H_2 are in excellent agreement with an expression for the rotational state-specific rate coefficients for this reaction derived by Gerlich *et al.*²¹ as an empirical approximation to their statistical phase space calculations. This agreement supports the prediction of these calculations that rotational excitation of the neutral reactant enhances the rate coefficient by lowering the effective energy barrier to reaction.

More direct evidence concerning the role of reactant internal energy upon reactivity was obtained by comparing the thermal rate coefficients measured in the present study with previously published drift tube and guided ion beam results on the translational energy dependence of the rate coefficients. This comparison not only demonstrated that reactant rotational energy and translational energy are equally effective in promoting reaction, but has also allowed rate coefficients to be derived for the reactions of $C^+(^2P)$ with H_2 and D_2 in the $v=1$ vibrational state.

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