Reaction of $C^+(^4P)$ with Molecular Hydrogen

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Introduction

The reaction of the ground state $C^+(^2P_u)$ ion with molecular hydrogen to form CH^+ has been studied experimentally and computationally at a number of laboratories.¹⁻⁸ Since this reaction appears to have considerable interest it was thought worthwhile to extend the study to the corresponding reaction involving the first excited state of C^+ . The dynamics of relatively few reactions involving electronically excited projectiles have been studied.^{9,10} In the case of C^+ the ground state reaction with H_2 is endothermic by 0.42 eV whereas the excited state reaction is exothermic, consequently at center of mass energies below 0.42 eV the excited state reaction can be investigated without interference from the ground state reaction. Actually the details of the kinematics of these two reactions are such that the energies of the resulting products (CH^+) are sufficiently different so that one can separate the two reactions over a wide range of energies. In this publication we wish to report on the investigation of the reaction of the $C^+(^4P_g)$ ion with molecular hydrogen over an energy range of 0.5 eV to 9 eV in the laboratory system.

Experimental

The apparatus used in this study was described previously.¹¹ The instrument consists of two quadrupole mass filters and two hemispherical analyzers in tandem. The first quadrupole and electrostatic analyzer

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and their associated lens system prepare a mass analyzed projectile ion beam of known energy and focus it into a reaction chamber containing the reactant gas whose pressure is measured with an MKS Baratron. The reaction cell consists of two concentric cylinders, the inner cylinder being able to rotate through $\pm 45^\circ$. The axis for the angular movement of the detection system passes through the center of the reaction cell. The detection system consisting of the second mass filter, electrostatic analyzer and the associated lens system moves in a planar direction pivoting the inner cylinder as the system is moved by a mechanical feed-through. Ions passing through the secondary quadrupole strike a Bendix continuous channel electron multiplier. Pulse counting techniques are used. The data for the angular and energy distributions for the reactant and product ions are collected, stored and processed using a PDP-8/E mini-computer. The C^+ ion beam is prepared by electron bombardment of CO. Attenuation studies of the resulting beam indicate that about 6% of the beam is in the 4P_g state and the remainder in the ground state. Energy calibration of the instrument in the low energy region is realized by studying the charge transfer reaction between Ar^+ and Ar and assuming that the product Ar^+ has a thermal energy.

Results and Discussion

A typical energy spectrum for the reaction $C^+(H_2,H)CH^+$ is given in Figure 1 where the yield of CH^+ is plotted as a function of projectile ion lab energy. The peak on the extreme right is the CH^+ arising from the reaction of $C^+(^4P_g)$, the narrow peak in the center is the $^{13}C^+$ component of the projectile ion beam, which is included for comparison purposes, and the broad peak on the left is CH^+ arising from ground state $C^+(^2P_u)$ ion reactions.

In order to verify the electronic states contributing to the two peaks in Figure 1, the electron bombardment energy and the relative energy of interaction were varied. As the relative energy was decreased below the threshold for the ground state $C^+(^2P_u)$ reaction the peak on the left disappeared as expected.

The high energy peak of CH^+ showed a strong dependence upon electron energy in the range of 23 eV to 41 eV. At 23 eV the high energy peak was not present. As the electron energy was raised the relative intensity of the high energy peak to the low energy peak continued to increase up to 160 eV, the highest electron energy used in this work. The appearance potential of $C^+(^2P_u)$ from CO is 20.89 eV.¹² The $C^+(^4P_g)$ state is 5.33 eV above the ground state C^+ ion.¹³ There are other excited states of C^+ but these states decay directly or cascade to the 4P or 2P states in less than 10^{-7} seconds.¹⁴ Thus, it is unlikely that any other states of C^+ contribute to product formation. This is further substantiated by the attenuation measurements of C^+ in N_2 gas indicating that only two states are present.

INSERT #1 → Frequently the limiting value of the exoergicity (Q), which is the difference between the kinetic energy of products and reactants, is used to determine the state of the final ionic product. However, the three lowest potential energy curves of $CH^+(\tilde{X}^1\Sigma^+, a^3\Pi$ and $A^1\Pi)$ have the same asymptotic limit [$C^+(^2P_u) + H(^2S_g)$]. (See Table II.) Also, the $CH^+(b^3\Sigma^-)$ state lies 0.5 eV above the asymptotic limit of the lower three states. Q for the reaction measured here is approximately 0.9 eV over the entire energy range studied. This limit is consistent with the asymptotic value of all three lowest states and appears to eliminate the $CH^+(b^3\Sigma^-)$ state as a possibility. Of course, the limiting value of Q cannot tell us in

which one of these three states the ionic product resides. The value of Q was calculated in the customary manner using the principles of conservation of energy and momentum and the measured kinetic energy of the product ion (CH^+). In Figure 2 the CH^+ ion velocity distribution in the center of mass Cartesian coordinate system is illustrated for a C^+ laboratory energy of 8 eV. The circle designated Q2 corresponds to the asymptotic limit for the three lower states mentioned above. Q1 corresponds to the maximum Q (and thus velocity) of $b^3\Sigma^-$ state. It is possible that the $\text{CH}^+(b^3\Sigma^-)$ state which is not excluded by spin and symmetry considerations (Table 1) is present since the lowest contour lines fall within the allowed velocity distribution range. However, there is no observable asymmetry in the velocity profile of the CH^+ ions indicated in Figure 2. ⁵ ~~Studies at the relative energies~~ below the thermodynamic threshold for the ground state reaction gave no evidence of $\text{CH}^+(b^3\Sigma^-)$ being present near the center of mass velocity. The overlap of the contour lines into the $b^3\Sigma^-$ state region probably results from the broadening caused by the thermal motion of the target gas, finite C^+ beam width (in this case 0.1 eV) and finite instrument resolution.

In order to get some indication of the electronic state of the CH^+ product we considered the spin and symmetry conservation of this system and the results are given in Tables 1 and 2. Examination of these tables ^{and figures} shows that of the three states consistent with our measured limiting Q value only the $a^3\Pi$ state can conserve both spin and symmetry. Consequently we assume that the reaction in our energy domain can be represented by the equation

However, the reaction does not proceed along a smooth lowest energy $^4\Pi$ surface of the intermediate C--H-H^+ . Preliminary ab-initio configuration interaction calculations performed some years ago¹⁵⁻¹⁷ in support of an experimental study of the reaction $\text{C}^+ + \text{H}_2$ combined with symmetry and spin restrictions indicated that the reactants $\text{C}^+(\text{}^2\text{P}_u) + \text{H}_2(\tilde{\text{X}}^1\Sigma_g^+)$ combined to form $^2\Sigma^+$ and $^2\Pi$ states of the $\text{C}^+\text{--H-H}$ complex in linear symmetry (correlating to the $^2\text{A}'$, $^2\text{A}' + ^2\text{A}''$ states of the intermediate complex in C_s symmetry and to the $^2\text{B}_2$, $^2\text{A}_1 + ^2\text{B}_1$ states in C_{2v} symmetry). Those configuration interaction calculations also showed that the lowest $^2,4\Sigma^-$ and the $^4\Pi$ states as well as the second root of the $^2\Pi$ state of the C--H-H^+ complex dissociated smoothly to the same asymptotic limit $\text{C}(\text{}^3\text{P}_g) + \text{H}_2^+(\tilde{\text{X}}^2\Sigma_g^+)$ and that at higher energies at the asymptotes were second roots of the $^4\Sigma^-$ and $^4\Pi$ states of the $\text{C}^+\text{--H-H}$ complex arising from the reactants $\text{C}^+(\text{}^4\text{P}_g) + \text{H}_2(\tilde{\text{X}}^1\Sigma_g^+)$. Thus, the lowest energy $^4\Pi$ state of the intermediate complex correlating to $^4\text{A}' + ^4\text{A}''$ in C_s symmetry and to $^4\text{B}_2 + ^4\text{A}_2$ in C_{2v} symmetry arises from $\text{C}(\text{}^3\text{P}_g) + \text{H}_2^+(\tilde{\text{X}}^2\Sigma_g^+)$ rather than from $\text{C}^+(\text{}^4\text{P}_g) + \text{H}_2(\tilde{\text{X}}^1\Sigma_g^+)$.

In addition our configuration interaction calculations for the product channels $\text{CH}^+ + \text{H}$ (or $\text{CH} + \text{H}^+$) indicated that the $^4\Pi$ state of the C--H-H^+ intermediate which was lowest in the equilibrium region and which arose from $\text{C}(\text{}^3\text{P}_g) + \text{H}_2^+(\tilde{\text{X}}^2\Sigma_g^+)$ tended to start to dissociate toward high lying products H and the $^3\Pi \text{CH}^+$ state arising from $\text{C}(\text{}^3\text{P}_g) + \text{H}^+(\text{}^1\text{S}_g)$. The second $^4\Pi$ state in the equilibrium region appeared to undergo a possible avoided crossing in an intermediate region with another $^4\Pi$

state and then the lower branch tended to dissociate toward the lowest energy pair of permitted dissociation products $\text{CH}^+(\text{a}^3\Pi) + \text{H}(\text{S}_g^2)$. $\text{CH}^+(\text{a}^3\Pi)$ arises from $\text{C}^+(\text{P}_u^2) + \text{H}(\text{S}_g^2)$, $\text{C}^+(\text{P}_g^4) + \text{H}(\text{S}_g^2)$ give rise to $\text{CH}^+(\text{3,5}\Sigma^+)$ and $\text{3,5}\Pi$ states). Hence it appears mechanistically logical that the second $^4\Pi$ state of the C--H-H^+ intermediate arose from the $\text{C}^+(\text{P}_g^4) + \text{H}_2(\tilde{\text{X}}^1\Sigma_g^+)$. This intermediate would then have dissociated diabatically to $\text{H} + \text{CH}^+$ either to the third $^3\Pi$ state or to a $^5\Pi$ state of CH^+ - but not to both states. As we have previously pointed out¹⁶⁻¹⁹ there is a uniqueness theorem which insures that while separated fragments can correlate to one or several intermediate states depending on their spin and symmetries, once in a particular state there is one and only one unique set of dissociation asymptotic products. This can be mitigated by curve crossing but any curve can lead only to one set of separated products.

However, this second $^4\Pi$ state in the equilibrium region then underwent an avoided crossing with another repulsive $^4\Pi$ curve in an intermediate distance region and tended toward dissociation to $\text{CH}^+(\text{a}^3\Pi) + \text{H}$. There must yet be another curve crossing further out toward the dissociation asymptote of this $^4\Pi$ state with the $^4\Pi$ state which is lowest in energy in the equilibrium region. Since these curves will cross steeply and there is excess internal energy on the repulsive curve, there is considerable possibility of remaining on the diabatic surface of the repulsive curve giving rise to products $\text{CH}^+(\text{a}^3\Pi) + \text{H}$. While the above discussion invokes only the symmetries of the linear intermediates for simplicity and discusses the problem in terms of curves and curve crossings the basic arguments are unchanged if one considers the C_s or C_{2v} symmetries or discusses the problem in terms of more general surfaces and surface crossings. /

We assume, therefore, that the product ion for the excited C^+ reaction is in the $a^3\Pi$ state. So, the internal energy of the CH^+ product is given by $-Q - \Delta H_0 + U_R$ and is represented by the squares ($\square$) and the translational energy of the products (CH^+ and H) by the circles ($\circ$) in Figure 3. The solid line in the upper portion of this figure gives the total energy available (heat of reaction plus relative kinetic energy). At low kinetic energies about 25% of the heat of reaction goes into translational energy of the products and 75% goes into internal energy (vibration and rotation). In view of the small reduced mass of this system and assuming a moderate reaction cross section conservation of angular momentum indicates a relatively small spread in permitted rotational quantum numbers²⁰ for the product and hence one expects that the bulk of the 3 eV is in the form of vibrational energy. This is further supported by measurements on the product energy line width. Using a projectile ion beam with an energy spread of 70 meV (FWHM) the product ion line width in the energy spectrum was only 0.26 eV (FWHM) when the projectile ion had 4 eV energy (lab). We interpret this as indicating that the portion of the heat of reaction deposited in the internal energy of CH^+ resides in a relatively few high lying vibrational levels close to the dissociation limit and the vibrational population is highly inverted. It will also be noted that the product relative energy is increasing with projectile ion kinetic energy at about the same rate that the total available energy is increasing suggesting that the total available kinetic energy of the projectile is going into kinetic energy of the products.

Figure 2 supports this conclusion since it shows that the product ion has maximum internal energy possible and the translational energy is peaked well ahead of the center of mass supporting a direct mechanism for the reaction with the "complex" living for a time significantly less than

10^{-12} sec. This conclusion is consistent with Figure 1 where the energy of the product peak is well forward not only of the energy of the center of mass of the system but also well ahead of the position expected for spectator stripping point.

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Table I (continued)

A. Reactants $C^+ + H_2$ (or $C + H_2^+$)^b(eV Energy
Relative to
Separate Neutral
Atoms)

Table I (continued)

 $\text{CH}^+ \text{--H}$ (or $^+\text{CH--H}$ or CH--H^+)

Spin and Symmetry Restrictions

(eV) Energy
Relative to
Separate Neutral
AtomsB. Products $\text{CH}^+ + \text{H}$ (or $^+\text{CH} + \text{H}$ or $\text{CH} + \text{H}^+$)^b

Table I (continued)

B. Products $\text{CH}^+ + \text{H}$ (or $^+\text{CH} + \text{H}$ or $\text{CH} + \text{H}^+$)^b(eV) Energy
Relative to
Separate Neutral
Atoms

Table I (continued)

(eV) Energy
Relative to
Separate Neutral
Atoms

B. Products $\text{CH}^+ + \text{H}$ (or $^+\text{CH} + \text{H}$ or $\text{CH} + \text{H}^+$)^b

Table I (continued)

B. Products $\text{CH}^+ + \text{H}$ (or $^+\text{CH} + \text{H}$ or $\text{CH} + \text{H}^+$)^b(eV) Energy
Relative to
Separate Neutral
Atoms

Table I (continued)

B. Products $\text{CH}^+ + \text{H}$ (or $^+\text{CH} + \text{H}$ or $\text{CH} + \text{H}^+$)^b(eV) Energy
Relative to
Separate Neutral
Atoms

Table I (Continued)

^aThe subscripts (g) or (u) in parentheses would refer to the linear complex of $D_{\infty h}$ symmetry; for $C_{\infty v}$ symmetry this subscripts on parentheses carry extra pseudosymmetry information necessary to trace uniquely through intermediates of C_s symmetry to those of C_{2v} symmetry.

^bThe + sign is placed on the atom on which it would reside in the totally separated atom limit. This enables one to follow more clearly the diabatic pathways.

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Table II

 CH^+ Spin and Symmetry Restrictions^b

				Energy Relative To Separated Neutral Atoms
C^+	+	H	$\rightarrow$	^+CH 11.264
$2p_u$		$2s_g$		$1,3_{\Sigma}^+, 1,3_{\Pi}$
C	+	H^+	$\rightarrow$	CH^+ 13.598
$3p_g$		$1s_g$		$3_{\Sigma}^-, 3_{\Pi}$
C	+	H^+	$\rightarrow$	CH^+ 14.862
$1d_g$		$1s_g$		$1_{\Sigma}^+, 1_{\Pi}, 1_{\Delta}$
C	+	H^+	$\rightarrow$	CH^+ 16.282
$1s_g$		$1s_g$		1_{Σ}^+
C^+	+	H	$\rightarrow$	^+CH 16.598
$4p_g$		$2s_g$		$3,5_{\Sigma}^-, 3,5_{\Pi}$

^bSee footnote b in Table I

FIGURE CAPTIONS

Figure 1 - Energy spectrum of CH^+ arising from the reaction $\text{C}^+(\text{H}_2, \text{H})\text{CH}^+$ at a C^+ lab energy of 8 eV.

Figure 2 - CH^+ ion velocity distribution in the center of mass Cartesian coordinates for a C^+ laboratory energy of 8 eV. Q1, Q2, and Q3 denote respectively the maximum allowable velocity for $\text{b}^3\Sigma^-$ products, the minimum allowable velocity for $\text{a}^3\Pi$ products, and the maximum allowable velocity for $\text{a}^3\Pi$ products. The dashed circle denotes the 50% profile of the C^+ primary beam and the cross indicates the position of the center of mass.

Figure 3 - Distributed energy vs. C^+ laboratory energy. Internal energy of $\text{CH}^+(\square)$, translational energy of the products CH^+ and $\text{H}(0)$. The solid line represents the total energy available, i.e., heat of reaction plus relative kinetic energy.

Figure 4
Schematic potential energy curves for the reaction $\text{C}^+ + \text{H}_2$ (or $\text{C} + \text{H}_2^+$). Potential energy (E) is plotted versus the C-H distance ($R_{\text{C-H}}$) for linear configuration of reactants. $R_{\text{H-H}}$ is held constant

Figure 5
Schematic potential energy curves for $\text{CH}^+ + \text{H}$ (or $\text{CH} + \text{H}^+$). Potential energy (E) is plotted versus the H-H distance ($R_{\text{H-H}}$) for a linear configuration. $R_{\text{C-H}}$ is held constant

FIG. 1