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International Journal of Mass Spectrometry 195/196 (2000) 491–505

International Journal of Mass Spectrometry

The $C_2H_7^+$ potential energy surface: a Fourier transform ion cyclotron resonance investigation of the reaction of methyl cation with methane

J.J. Fisher, G.K. Koyanagi, T.B. McMahon*

Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Received 14 September 1999; accepted 27 September 1999

Abstract

Fourier transform ion cyclotron resonance experiments have been carried out to probe the nature of the potential energy surface for the reaction of methyl cation (CH_3^+) with methane (CH_4) to give the ethyl cation ($C_2H_5^+$). Product distributions for reactions of CH_3^+ and CD_3^+ with CD_4 and CH_4, respectively, are found to give a near statistical distribution of ethyl cation products, in good agreement with previous work. When the methyl cation is initially coordinated to HF in the form of a methylfluoronium ion, however, the product distributions are decidedly nonstatistical and are indicative of a reaction which is very nearly thermoneutral. Thermochemical data for relevant species suggest that the reaction is very slightly endothermic. All of the experiments support the intermediacy of a $C_2H_7^+$ complex in the reactions. Ab initio calculations, in conjunction with all of the experimental data, reveal that there are likely three different stable forms of $C_2H_7^+$ involved in the potential energy surface for the reaction. One of the forms, a nonclassical $C_2H_5^+$ coordinated to H_2 in a proton bound dimerlike structure, has not previously been considered to play a role in this reaction. The existence of this structure is supported by infrared multiphoton dissociation experiments on $C_2H_7^+$ previously carried out by Lee and co-workers (J. Am. Chem. Soc. 111 (1989) 5597) and the high pressure mass spectrometric experiments of Hiraoka and Kebarle (J. Am. Chem. Soc. 98 (1976) 6119). (Int J Mass Spectrom 195/196 (2000) 491–505) © 2000 Elsevier Science B.V.

Keywords: $C_2H_7^+$; FTICR; Methylation of methane

1. Introduction

The reactions of methyl cation and methane radical cation with methane, Eq. (1), occupy a venerable position in the history of gas phase ion chemistry [1]. Aside from the very early observation of the reaction of the hydrogen molecular ion with hydrogen [2,3], Eq. (2), they are the first ion molecule reactions that were systematically studied. These reactions also have in common the fact that they all give rise to ionic products with nonclassical structures involving three center two electron bonds.

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \tag{1a}$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \tag{1b}$$

$$H_2^+ + H_2 \rightarrow H_3^+ + H \tag{2}$$

A great deal of work has been carried out attempting to elucidate the details of the mechanism by which the CH_3^+ cation reacts with CH_4. The two possibilities proposed, a direct mechanism [4] and a complex

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* Corresponding author.

Dedicated to Bob Squires for his many seminal contributions to mass spectrometry and ion chemistry.

PII S1387-3806(99)00231-6

mechanism involving a $C_2H_7^+$ intermediate [5], have been examined by a wide variety of experimental techniques. The earliest study by Wexler and Jesse [6] using elevated methane pressures in the ion source of a mass spectrometer implicated the intermediacy of $C_2H_7^+$ in the reaction of CH_3^+, Eq. (3).

$$\begin{array}{l} CH_3^+ + CH_4 \rightarrow [C_2H_7^+]^* \rightarrow C_2H_5^+ + H_2 \\ \qquad\qquad\qquad\quad \downarrow CH_4 \\ \qquad\qquad\qquad\quad C_2H_7^+ \end{array} \tag{3}$$

This was also supported by the work of Field, Franklin, and Munson [7] who demonstrated a third-order dependence of $C_2H_7^+$ production on CH_4 pressure, consistent with collisional stabilization of an excited $C_2H_7^+$ intermediate. Also in support of the complex mechanism, Abramson and Futrell [8] found that, in tandem mass spectrometric experiments involving reaction of CH_3^+ (CD_3^+) with CD_4 (CH_4) at low collision energies, there was apparently complete statistical scrambling of hydrogen and deuterium between the ionic and neutral products. These results thus strongly suggested a long lived $C_2H_7^+$ intermediate in which all of the hydrogens become equivalent.

In contrast to these experiments, crossed beam studies by Wolfgang and co-workers [9] concluded that, on the basis of the strong forward scattering of the products, no persistent complex of lifetime greater than 10^{-12} s was involved in $C_2H_5^+$ formation. Weiner et al. [10] also carried out crossed beam experiments using deuterium isotopic variants of the reactants, Eqs. (4) and (5), with the conclusion that there is no evidence to support the formation of a long lived intermediate. There was, however, an increasing tendency for nonrandom H, D distributions in the products at increased collision energies, leading these authors to postulate the existence of a short lived $C_2H_7^+$ intermediate. Huntress [11], using ion cyclotron resonance (ICR) techniques, and Lee, Bierbaum and DePuy [12], using flowing afterglow techniques, have also investigated the thermal energy reactions of deuterium labelled methyl cations with labelled and unlabelled methanes. In both cases slightly nonstatistical H/D scrambling in the ethyl cation products was observed. On the basis of the nonstatistical hydrogen losses, the latter authors conjectured that an isotope effect was present in the dissociation of the $C_2H_7^+$ intermediate, which represented the rate determining step in the reaction. However, since the reaction forming $C_2H_7^+$ is 41 kcal mol^{-1} exothermic, this amount of energy is available in the intermediate and it is thus difficult to rationalize an isotope effect of this magnitude on the basis of simple zero point energy considerations. Rather, these authors concluded that incomplete scrambling of hydrogen and deuterium was occurring during the lifetime of the $C_2H_7^+$ intermediate.

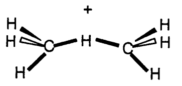
$$CH_3^+ + CD_4 \longrightarrow \begin{cases} C_2H_3D_2^+ + D_2 & (4a) \\ C_2H_2D_3^+ + HD & (4b) \\ C_2HD_4^+ + H_2 & (4c) \end{cases}$$

$$CD_3^+ + CH_4 \longrightarrow \begin{cases} C_2H_4D^+ + D_2 & (5a) \\ C_2H_3D_2^+ + HD & (5b) \\ C_2H_2D_3^+ + H_2 & (5c) \end{cases}$$

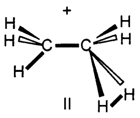
The existence of two different stable forms of $C_2H_7^+$ has been definitively demonstrated by Hiraoka and Kebarle [13] in high pressure mass spectrometric (HPMS) experiments. Operating at low temperatures in H_2 to which trace amounts of methane had been added, clustering equilibrium between $C_2H_5^+$ and H_2 was observed to lead to a weakly bound form of $C_2H_7^+$, II. The temperature dependence of the equilibrium, (6), leads to a binding energy of 4.0 kcal mol^{-1} and an association entropy of -19.6 cal mol^{-1} K^{-1}. The low value of

$$C_2H_5^+ + H_2 \rightarrow C_2H_7^+ \tag{6}$$

the entropy of association, is consistent with a loosely bound complex with a considerable degree of freedom, possibly even a free rotation of the H_2 within the complex. At higher temperatures the equilibrium was observed to become much more favourable, presumably as the result of formation of a second, more stable, form of $C_2H_7^+$, I, which has a barrier to its formation from II, which is overcome as the temperature is raised. This second form of the ion was found to be bound by 11.8 kcal mol^{-1} with an association entropy of -25 cal mol^{-1} K^{-1}. A more recent HPMS study of this higher temperature clustering equilibrium in our own laboratory resulted in a ΔH° of association of -12.8 kcal mol^{-1} and a corresponding ΔS° of -27.5 cal mol^{-1} K^{-1} [14]. Either of these latter entropy changes is of a magnitude more normally observed in the association of polyatomic ions with neutral molecules and suggests that a more covalently bound complex has been formed with considerably less internal freedom than that in II. The structures assigned to these species, suggested at the time by low level ab initio calculations [15], were a C–C protonated ethane for I and a C–H protonated ethane for II.



I



II

Later calculations at a higher level of theory [16] reaffirmed these structural assignments and provided more accurate details of the bonding. The calculated binding enthalpy of I with respect to $C_2H_5^+$ and H_2, which included zero point energy corrections, of 7.4 kcal mol^{-1} agreed reasonably well with the experimental values of 11.8 and 12.8 kcal mol^{-1}.

More recently, Carneiro et al. [17] have carried out an extensive ab initio investigation of the details of the $C_2H_7^+$ potential energy surface at a very high level of theory. Once again, these calculations demonstrate that the C–C protonated form, I, is more stable than the C–H protonated form, II. The analysis of the clustering energetics, which included zero point energy and thermal corrections, gave values of ΔH°_{298} for formation of I and II from $C_2H_5^+$ and H_2 of -10.6 kcal mol^{-1} and -6.2 kcal mol^{-1}, respectively. Thus, relative to the experimental HPMS values the binding of I is weaker while the binding of II is stronger, in both cases by ~2 kcal mol^{-1}. The calculated entropy change for formation of I of -25.2 cal mol^{-1} K^{-1} is in excellent agreement with both HPMS determinations of this quantity of -25 cal mol^{-1} K^{-1}. However, the calculated entropy change for formation of II of -26.7 cal mol^{-1} K^{-1} is not in good agreement with the experimental value of -19.6 cal mol^{-1} K^{-1}. Other features of this calculated potential energy surface also appear to be inconsistent with experimental observations. First, the ab initio calculations give a barrier of 2.9 kcal mol^{-1} for the transition state connecting separated nonclassical $C_2H_5^+$ and H_2 with II. If II were the species observed at low temperature in the HPMS experiments then such a barrier would prevent its formation. Second, the calculations show no barrier between I and II in excess of the energy of separated nonclassical $C_2H_5^+$ and H_2. Again, if this were the case, then it would not have been possible to form II at any temperature in the HPMS experiments since the reactant $C_2H_5^+$ and H_2 would pass directly to I. Thus, although experiment and theory agree on the existence of (at least) two stable minima on the $C_2H_7^+$ surface, there are both energetic and dynamic details which are not well explained by this latest high level ab initio calculation.

The accuracy of the experimental and theoretical clustering energetics can be gauged from the agreement between the value of $\Delta H^\circ_f(C_2H_7^+)$ obtained from the accurately known values for $\Delta H^\circ_f(C_2H_5^+)$ [18,19] and $\Delta H^\circ_f(H_2)$ and the proton affinity of C_2H_6 [14,20]. Several experiments involving the appearance energies of $C_2H_5^+$ from a variety of ethyl halides, C_2H_5X [18,19], have led to a value of $\Delta H^\circ_f(C_2H_5^+)$ of 215.3 kcal mol^{-1}. When this is combined with the clustering enthalpy [14] of -12.8 kcal mol^{-1} obtained in our laboratory, a value of $\Delta H^\circ_f(C_2H_7^+)$ of 202.5 kcal mol^{-1} is derived. Correspondingly, when the proton affinity of C_2H_6 of 142.7 kcal mol^{-1} is used $\Delta H^\circ_f(C_2H_7^+)$ is calculated as 202.8 kcal mol^{-1}. The excellent agreement between these two values, independently obtained, indicates that the $C_2H_7^+$ species obtained by addition of $C_2H_5^+$ to H_2 above room temperature in the high pressure mass spectrometer is very likely the same as that obtained by protonation of C_2H_6.

In a series of extremely elegant experiments Lee and co-workers [21] have used consequence spectroscopy to demonstrate that two different isomeric forms of $C_2H_7^+$ can also be generated in a corona discharge in dilute C_2H_6–H_2 mixtures which are allowed to undergo a supersonic expansion and then to pass through a skimmer into the acceleration region of a magnetic sector mass spectrometer. The low rotational temperature of the expansion (<40 K) permits the formation and persistence of the weakly bound form of $C_2H_7^+$. Vibrational spectra were obtained by varying the wavelength of laser irradiation while observing the extent of dissociation of $C_2H_7^+$ and the appearance of $C_2H_5^+$. Two distinctly different vibrational spectra in the 2400–4200 cm^{-1} region were observed and assigned to the structures I and II above. While the agreement between experimentally observed bands and ab initio harmonic vibrational frequencies calculated by Dupuis [22] were very good for structure I, the agreement was considerably less satisfactory for II. In particular, the theoretical calculation predicted a stretching frequency for the H–H bond which was apparently too low by $\sim$450 cm^{-1}. However, based on correlations of the red shift of the H–H stretching frequency with interaction energy in H_n^+ clusters [23] these authors concluded that the interaction between $C_2H_5^+$ and H_2 in I must be $\sim$4 kcal mol^{-1} which is in excellent agreement with the value obtained at low temperature in the HPMS experiments. As noted above, the vibrational analysis in the ab initio calculations of Carneiro et al. [17] also permitted a calculation of the entropy changes. The vibrational frequencies obtained for I agree extremely well with those obtained from the infrared photodissociation experiments of Lee and co-workers [21] for their warmer expansion conditions. However, the frequencies obtained for II are not consistent with the observations obtained from the colder expansion. Most notably, in agreement with earlier calculations by Dupuis [22], cited by Lee and co-workers [21], no frequency above 3100 cm^{-1} is obtained, whereas a strong feature at 3964 cm^{-1} was experimentally observed. Thus the photodissociation experiments implicate a $C_2H_7^+$ species with a weaker bond between ethyl cation and H_2 which would have a more intact H_2 molecule having a vibrational frequency more closely resembling that in free H_2.

Very recently Heck, de Koning, and Nibbering [24] have observed an ambident reactivity of the $C_2H_7^+$ ion. In favourable circumstances both methyl cation transfer as well as proton transfer were seen, although the occurrence of slow, endothermic proton transfer at a rate comparable to that for exothermic methyl cation transfer indicated that either the reacting $C_2H_7^+$ contained excess energy (either kinetic or internal) or the methyl cation transfers are, in many cases, accompanied by a significant internal barrier. In experiments involving isotopically labelled species complete scrambling within the $C_2H_7^+$ occurred and the authors concluded that this must be via a [CH_3^+, CH_4] loosely bound ion-neutral complex since the "classical" structure, II, which would readily permit this scrambling is energetically inaccessible according to the experimental data from $C_2H_5^+$–H_2 clustering. In addition, metastable dissociation experiments involving these isotopically labelled species showed exclusive loss of H_2 demonstrating that there is a substantial isotope effect associated with H_2 versus HD versus D_2 loss.

Previous experiments from this laboratory have shown that CH_3FH^+, formed by ion molecule reactions in CH_3F, is an effective methylating agent toward weak n-donor bases such as N_2, CO_2, Xe, and Kr [25–27]. In addition, however, a consideration of relevant thermochemistry suggests that the methyl cation affinity of CH_4 is also greater than that of HF and that therefore the σ-donor base methane might also be methylated by CH_3FH^+. An ab initio study of this reaction has been carried out by Branchadell et al. [28] at the MP2/6-31G* level. They found that the methylation of methane by CH_3FH^+ involves a transition state which is predicted to be 13 kcal mol^{-1} above the energy of separated reactants. Thus, if this is the case, even though the methylation reaction is exothermic it would not be observable under ICR conditions. However, as demonstrated below, this reaction does proceed rapidly at thermal energies and thus must involve no significant barrier to the formation of either $C_2H_7^+$ or $C_2H_5^+$ and H_2.

In the present study the results of experiments in which $C_2H_7^+$ has been generated at low pressures in a Fourier transform ion cyclotron resonance (FTICR) spectrometer by reaction of CH_3FH^+ with methane are presented. In addition isotopic variations of this reaction have also been carried out in which CH_3FH^+ is reacted with CD_4 and CD_3FH^+ is reacted with CH_4. The unusual isotope effect observed for these latter two processes also allows considerable insight into the $C_2H_7^+$ potential energy surface. These FTICR experiments have been combined with the existing ab initio calculations, HPMS clustering measurements, and infrared photodissociation experiments to propose a new potential energy surface for the $C_2H_7^+$ system.

2. Experimental

All FTICR experiments were carried out on a Bruker Spectrospin CMS 47 spectrometer which has been modified at the University of Waterloo by the addition of a high pressure external ion source. Both the essential features of the FTICR system and the high pressure external ion source have been described in detail elsewhere [29,30].

Clustering equilibria, proton transfer equilibria, and collision induced decomposition experiments were conducted on a reverse geometry double focusing mass spectrometer equipped with a high pressure ion source, also constructed at the University of Waterloo [31]. The instrument is configured around a commercial VG 7070 mass spectrometer which has been extensively modified by the addition and deletion of ion optics to function as a reverse geometry instrument. A series of ion optics and collision cell were installed in the region between the magnetic and electric sectors and direct pumping of this region by an 800 L/s diffusion pump was added. Collision induced dissociation mass spectra obtained by scanning the electrostatic analyser (ESA) voltage were acquired with an Ortec multichannel analyzer hardware and software system running on a PC.

Methyl fluoride was obtained from SCM Chemicals; methane, ethane, and hydrogen from Matheson Canada Ltd.; and methyl fluoride-d_3 and methane-d_4 from Merck Sharpe and Dohme Canada Ltd. All materials were used without further purification with the exception of multiple freeze-pump-thaw cycles.

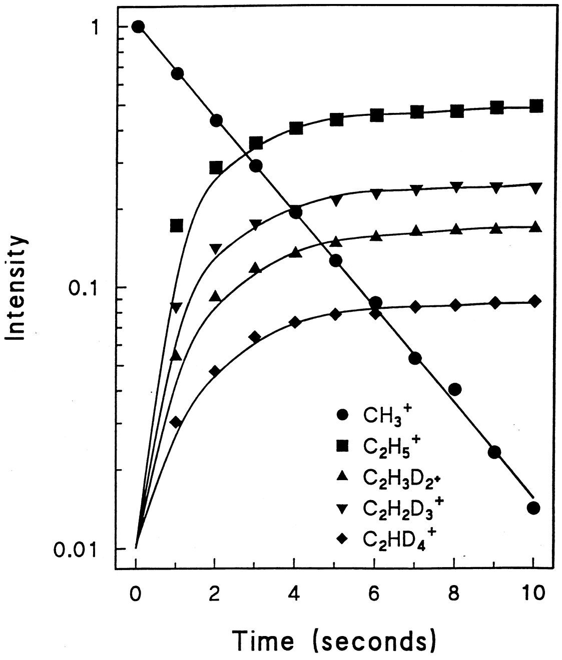


Fig. 1. Variation of relative ionic abundances as a function of time after isolation of CH_3^+ in a 1:1 mixture of CH_4 and CD_4 at a total pressure of 1.2×10^{-8} Torr.

3. Results and discussion

In order to compare the FTICR data acquired at very low pressures with that obtained using other techniques for the study of ion molecule reactions, the reactions of CH_3^+ and CD_3^+ with CD_4 and CH_4 were examined. The variation of relative ionic abundances with reaction time are shown in Figs. 1 and 2 for the two isotopic variants of the methyl cation reaction, Eqs. (4) and (5). The product distributions obtained from these experiments as well as those determined by Huntress [11] and Lee et al. [12], and those calculated for statistical losses, are summarized in Table 1. Weiner et al. [10] have previously presented a very convincing model for these isotopic reactions in which dissociation of the chemically activated $C_2H_7^+$ occurs from a pentacoordinate carbon structure (1,1 elimination) which presumably has the low temperature $C_2H_7^+$ structure, II; but at the same time hydrogen-deuterium scrambling in the chemically activated $C_2H_7^+$ protonated ethane structure, I, competes with unimolecular decomposition [Eq. (7)].

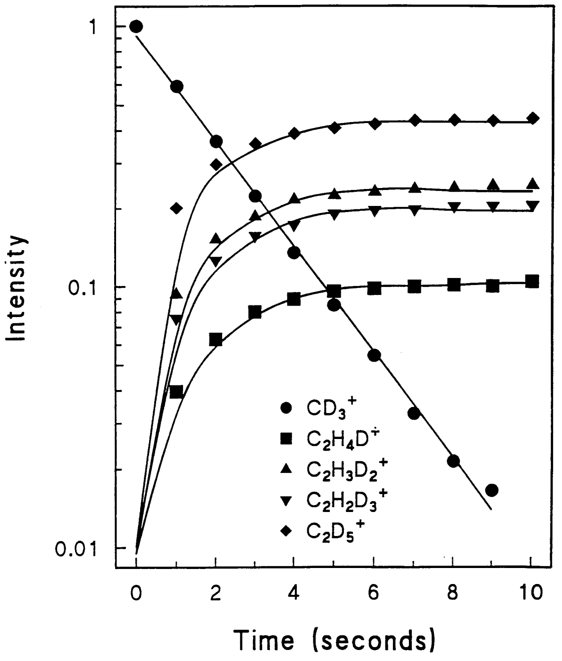


Fig. 2. Variation of relative ionic abundances as a function of time after isolation of CD_3^+ in a 1.5:1 mixture of CH_4 and CD_4 at a total pressure of 1.5×10^{-8} Torr.

$$\begin{array}{ll} CH_3^+ + CH_4 \rightarrow [C_2H_7^+(I)]^* \rightarrow [C_2H_7^+(II)]^* & \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow & (7) \\ \qquad\qquad\qquad\qquad\qquad C_2H_5^+ + H_2 & \end{array}$$

This model can serve to explain the slightly nonstatistical losses at thermal ion energy as well as the changing product distribution at higher ion energies. In addition, since the estimated lifetime of the complex was on the order of several vibrational periods but still shorter than the rotational period the pronounced forward scattering of products in crossed beam studies is also explained. This model is strongly supported by the present FTICR experiments, the conventional ICR experiments of Huntress [11], and the flowing afterglow data of Lee et al. [12]. In each of these low pressure experiments, for a short lived $C_2H_7^+$ complex, there is no possibility that collisional relaxation of the chemically activated species can take place and thereby alter the unimolecular dissociation lifetime. All three sets of data show that HD elimination is diminished relative to H_2 and D_2 losses based on statistical expectation which is consistent with a 1, 1 elimination mechanism and a lifetime of the complex in which each carbon still retains some memory of its nascent hydrogens or deuteriums. Thus, formation of the more stable species, I, renders the CH_3 and CD_3 groups initially equivalent in reactions (4) and (5). Scrambling occurs via interconversion of I and II, but 1,1 elimination from II competes with scrambling. The lifetimes of these two processes are such that nearly, but not complete, H/D scrambling occurs thus favouring H_2 and D_2 losses relative to HD loss since neither of the individual methyl groups initially contains both H and D.

A short lifetime of the $C_2H_7^+$ intermediate can be very readily rationalised from the now well established thermochemistry of the appropriate species. From the proton affinity of C_2H_6 [14,20] the ΔH_f° of

Table 1
Product distributions for the reaction of isotopic methyl cations with methane

Reaction		Huntress	Lee et al.	This work	Statistical
$CH_3^+ + CD_4$	$\rightarrow C_2H_3D_2^+ + D_2$	0.28	0.32	0.33	0.29
	$\rightarrow C_2H_2D_3^+ + HD$	0.50	0.50	0.49	0.57
	$\rightarrow C_2HD_4^+ + H_2$	0.22	0.18	0.18	0.14
$CD_3^+ + CH_4$	$\rightarrow C_2H_4D^+ + D_2$	0.17	0.15	0.18	0.14
	$\rightarrow C_2H_3D_2^+ + HD$	0.48	0.45	0.45	0.57
	$\rightarrow C_2H_2D_3^+ + H_2$	0.35	0.40	0.37	0.29

the more stable, C–C bridged, form of $C_2H_7^+$ is obtained as 202.8 kcal mol^{-1}. This, combined with $\Delta H^\circ_f(CH_3^+)$ of 261.3 kcal mol^{-1} [32] and $\Delta H^\circ_f(CH_4)$ of -17.9 kcal mol^{-1} [33] gives the internal excitation of the initially formed $C_2H_7^+$ as 40.9 kcal mol^{-1}. Taking the minimum energy required for dissociation of the more stable form of $C_2H_7^+$ to $C_2H_5^+$ and H_2 from our clustering experiments [14] as 12.8 kcal mol^{-1}, and adopting a simple Rice-Ramsperger-Kassel (RRK) model with a frequency factor of 10^{13} s^{-1} and 10 "active modes," allows calculation of an approximate upper limit for the unimolecular decomposition rate constant of $\sim 2 \times 10^{11}$ s^{-1}. Such a lifetime would just satisfy the requirements for H atom scrambling while retaining a forward peaked product distribution in the crossed beam experiments due to insufficient time for a full molecular rotation to occur. Alternatively for the less stable form of $C_2H_7^+$ with a minimum energy requirement of 4.0 kcal mol^{-1} for dissociation and an internal excitation of 28 kcal mol^{-1} a similar RRK calculation predicts a rate constant of $\sim 3 \times 10^{12}$ s^{-1}. Thus dissociation from either form is potentially compatible with the crossed beam data.

Apparently inconsistent with such a short lifetime are the observations by both Field, Franklin, and Munson [7] and Wexler and Jesse [6] who observed a stable $C_2H_7^+$ ion at elevated ion source pressures. In no case, however, was the pressure higher than 0.2 Torr and thus a chemically activated ion would necessarily have a lifetime of at least 5 ns to allow collisional stabilization to occur. In order to determine whether the persistent $C_2H_7^+$ present in these latter experiments was indeed due to collisional stabilization of a chemically activated adduct formed in reaction (3), we have examined the ion chemistry in pure methane in a high pressure mass spectrometer in our laboratory equipped with high resolution and collision induced decomposition capabilities. High resolution established that the ion at *m/z* 31 was, in fact, $C_2H_7^+$. Collision induced decomposition (CID) mass spectra of the $C_2H_7^+$ formed in pure methane and that formed from protonation of C_2H_6 were found to be identical. Examination of the variation of the relative ionic abundances with ion source residence time, shown in Fig. 3, revealed that the gradual increase in $C_2H_7^+$ intensity was not consistent with the very rapid disappearance of CH_3^+ but rather with the much slower disappearance of CH_5^+, possibly via Eq. (8), with an apparent rate constant of 5×10^{-14} cm^3 molecule^{-1} s^{-1}.

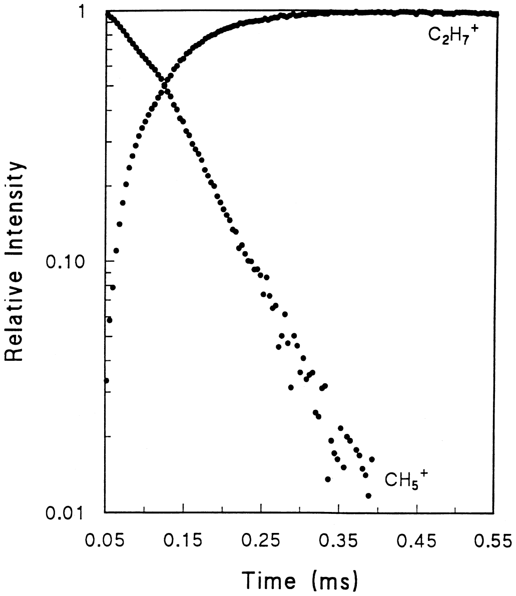


Fig. 3. Variation of relative ionic abundances of CH_5^+ and $C_2H_7^+$ in pure CH_4 in a high pressure ion source at a pressure of 6 Torr and a temperature of 50 °C.

$$CH_5^+ + CH_4 \rightarrow C_2H_7^+ + H_2 \quad (8)$$

This reaction could be viewed as a methyl cation transfer from the weaker base, H_2, to the stronger base, CH_4. However the possibility that this slow disappearance is due to exothermic proton transfer from CH_5^+ to C_2H_6 impurity in the methane must also be considered. When a liquid nitrogen trap was inserted in the gas flow line to the ion source the $C_2H_7^+$ peak disappeared from the mass spectrum at all reaction times. Therefore the appearance of $C_2H_7^+$ in the chemical ionization mass spectra of CH_4 does not implicate a long lived $C_2H_7^+$ intermediate in the reaction of CH_3^+ with CH_4 but, rather, a C_2H_6 impurity on the order of 50 ppm in the CH_4 [31].

The results obtained for the addition of CH_3^+ to CH_4 are markedly different when the CH_3^+ is initially

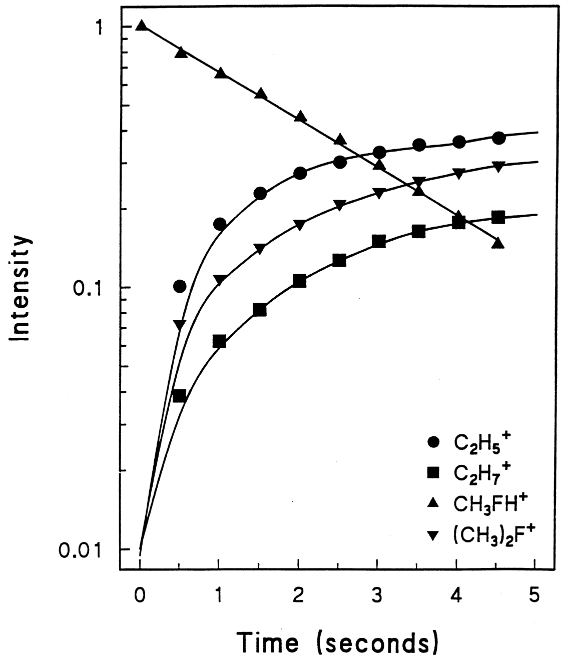


Fig. 4. Variation of relative ionic abundances as a function of time after isolation of CH_3FH^+ in a 12.5:1 mixture of CH_4 and CH_3F at a total pressure of 6×10^{-8} Torr.

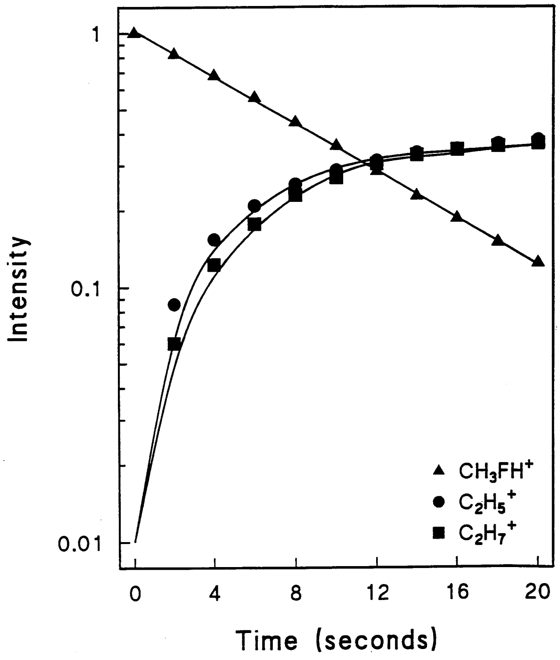


Fig. 5. Variation of relative ionic abundances as a function of time after isolation of CH_3FH^+ from a 1.5 ms pulsed valve addition of CH_3F to CH_4 in the FTICR cell at a pressure of 2.2×10^{-8} Torr.

coordinated to HF, in the form of CH_3FH^+. In this case, Eq. (9), both $C_2H_7^+$ and $C_2H_5^+$ are observed as products of reaction.

$$\mathrm{CH_3FH^+ + CH_4} \begin{cases} \rightarrow \mathrm{C_2H_7^+ + HF} & \text{(9a)} \\ \rightarrow \mathrm{C_2H_5^+ + H_2 + HF} & \text{(9b)} \end{cases}$$

$$\mathrm{CH_3FH^+ + CH_3F \rightarrow (CH_3)_2F^+ + HF} \qquad (10)$$

In addition, the ratio of these two products is very much dependent on the way in which the experiment is carried out. The variation of relative ionic abundances with reaction time for a 12.5:1 mixture of CH_4:CH_3F at a total pressure of 6×10^{-8} Torr is shown in Fig. 4. From these data, it is immediately apparent that production of $C_2H_5^+$ dominates over $C_2H_7^+$ at all times but, from a closer examination of these two abundances during the course of the reaction it is evident that, with increasing time, $C_2H_7^+$ represents an increasing fraction of the total product ion intensity, rising to a maximum of 0.5 of the $C_2H_5^+$ intensity at the longest times. However, the intensities of $C_2H_5^+$ and $C_2H_7^+$ together represent a constant fraction (0.68) of the total products of reaction of CH_3FH^+, Eqs. (9) and (10). This indicates that at increasing trapping time in the ICR cell a smaller fraction of the initially formed $C_2H_7^+$ is undergoing unimolecular decomposition to $C_2H_5^+$. An overall rate constant for reaction (9) of $1.8 \pm 0.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} is obtained indicating that roughly one collision in six of CH_3FH^+ with CH_4 is reactive. This phenomenon is even more readily apparent in the data shown in Fig. 5 in which CH_3F was pulsed into the ICR cell via a pulsed valve; CH_3FH^+ was isolated by standard ion ejection techniques and then allowed to react with CH_4 present at 2.2×10^{-8} Torr. Initially, $C_2H_7^+$ represents 0.44 of the total products of Eq. (9) but rises to 0.55 of the total at the longest trapping times. Thus, in this experiment, an even smaller fraction of the total $C_2H_7^+$ initially formed undergoes unimolecular decomposition. The *total* rate constant, $k_{(9a)} + k_{(9b)}$, found for the disappearance of CH_3FH^+ in this case is found to be $1.5 \pm 0.2 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Although the rate constants observed for the two types of experiments are, within experimental error, the same, the product distributions ($C_2H_7^+/C_2H_5^+$) are markedly different. These different product distributions may be understood from a consideration of the thermochemistry associated with Eq. (9) and the different manner in which CH_3FH^+ is formed in the separate experiments. Taking the proton affinity of CH_3F as 144 kcal mol^{-1} [34] reaction (9b) can be estimated to be 1.4 kcal mol^{-1} endothermic which is entirely consistent with the magnitude of the rate constant observed for $C_2H_5^+$ formation. Reaction (9a) is, however, exothermic by 11 kcal mol^{-1} and therefore no overall energetic impediment to its occurrence exists. From a thermal energy distribution of reactants it would then be expected that the higher energy end of the thermal energy distribution would lead to dissociation products, whereas the lower energy end of the distribution would give undissociated $C_2H_7^+$. If the CH_3FH^+ ion undergoing reaction contains some residual internal excitation from the manner in which it was formed then the rate constant for reaction (9b) will increase markedly as $C_2H_5^+$ becomes energetically accessible via unimolecular dissociation of the initially formed $C_2H_7^+$. The net observed rate constant, however, will remain unchanged with any change in internal energy as the initial rate determining step, formation of $C_2H_7^+$, is always exothermic. Thus only the product distribution and not the overall rate constant for reaction of CH_3FH^+ with CH_4 will change with internal energy of the reactant ion. In the first case CH_3FH^+ was generated by proton transfer from CH_5^+, Eq. (11), which is ~13 kcal mol^{-1} exothermic. Given the similar molecular size and structure of the two products

$$CH_5^+ + CH_3F \rightarrow CH_3FH^+ + CH_4 \qquad (11)$$

the reaction exothermicity may be estimated to be roughly equipartitioned giving an internal excitation in the initially formed CH_3FH^+ of ~6 kcal mol^{-1} which is sufficient to promote the occurrence of reaction (9a) at a substantial fraction of the collision rate. From the rate constant for Eq. (9) of ~1.6×10^{-10} cm^3 molecule^{-1} s^{-1}, and the calculated collision rate of 1.0×10^{-9} cm^3 molecule^{-1} s^{-1}, roughly one collision in six is reactive. Therefore, evidently collisions of CH_3FH^+ with CH_4 are relatively inefficient in relaxing the excess energy in the nascent ion, but the changing product ratio with increasing time does indicate that the energy content of CH_3FH^+ decreases as the number of collisions with CH_4 increases. In the pulsed valve experiment, CH_3FH^+ is formed by the reaction of CH_3F^+ with CH_3F, Eq. (12), which is also ~15 kcal mol^{-1} exothermic and which should also lead to an approximate equipartitioning of the excess energy. However, in this case, the pressure of CH_3F remains sufficiently high during the chemical ionization events that relaxation of the CH_3FH^+ by symmetric proton transfer, Eq. (13), can readily occur. In this way the excess internal energy should be relaxed to less than 1 kcal mol^{-1} within three collisions. Because the formation of the dimethyl-fluoronium ion, $(CH_3)_2F^+$, also occurs on one collision in three the relaxation of CH_3FH^+ should be 50% complete when the intensities of CH_3FH^+ and $(CH_3)_2F^+$ are equal and this was the condition established for the initial isolation of CH_3FH^+ in the present experiments.

$$CH_3F^+ + CH_3F \rightarrow CH_3FH^+ + CH_2F \qquad (12)$$

$$CH_3FH^+ + CH_3F' \rightarrow CH_3F'H^+ + CH_3F \qquad (13)$$

Due to signal/noise considerations it was not possible to work under conditions where a substantially larger fraction of the ions could be relaxed. It is evident from the significantly enhanced $C_2H_7^+:C_2H_5^+$ ratio, however, that more nearly thermalized ions are produced in this way compared to the method employing a static pressure of CH_3F and CH_4 in the ICR cell.

This model for reaction (9) in which $C_2H_7^+$ is formed with an internal excitation very close to the threshold for dissociation is also strongly supported by the dramatic isotope effect observed. Once again two different types of experiments were carried out. In the first, static mixtures of either CH_3F and CD_4 or CD_3F and CH_4 were employed, while in the second

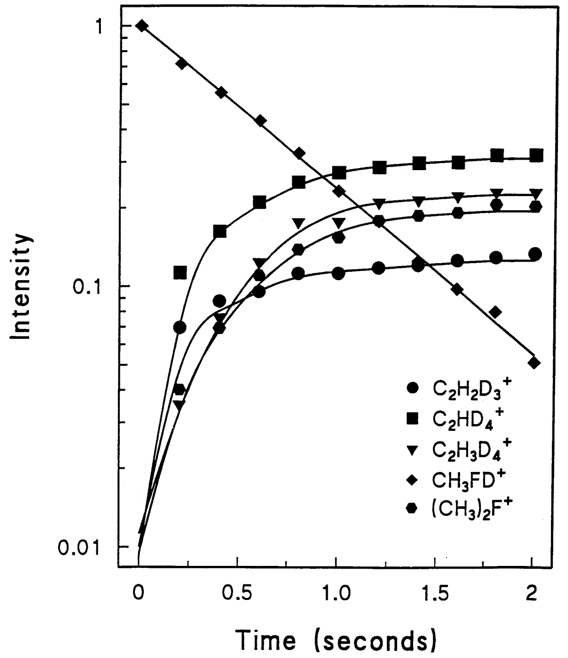


Fig. 6. Variation of relative ionic abundances as a function of time after isolation of CH_3FH^+ in a 20:1 mixture of CD_4 and CH_3F at a total pressure of 2.1×10^{-7} Torr.

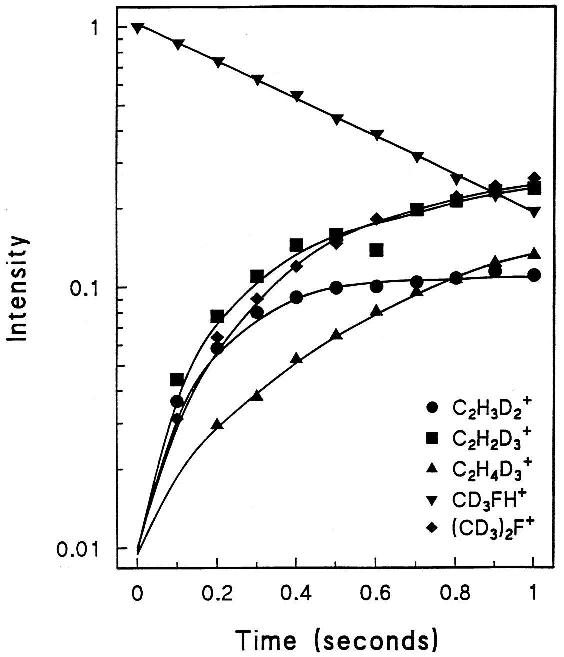


Fig. 7. Variation of relative ionic abundances as a function of time after isolation of CD_3FH^+ in a 18:1 mixture of CH_4 and CD_3F at a total pressure of 2.1×10^{-7} Torr.

CH_3F was pulsed into the ICR cell containing a static pressure of CD_4 in the ICR cell. The data obtained for the first type of experiment are shown in Figs. 6 and 7 and the corresponding product distributions given in Table 2. The reaction of CH_3FD^+ with CD_4 is found to have a rate constant of 1.7×10^{-10} cm^3 molecule^{-1} s^{-1} while the reaction of CD_3FH^+ with CH_4 is found to be slightly faster with a rate constant of 2.0×10^{-10} cm^3 molecule^{-1} s^{-1}. In both cases the analogue of the $C_2H_7^+$ product constitutes roughly 30% of the total reaction products with methane. Remarkably, in both cases the losses of H_2, HD, and D_2 are identical despite the fact that different numbers of hydrogens and deuteriums are involved in the two $[C_2H_7^+]$* intermediates. Thus, in these cases, the product distributions are decidedly nonstatistical and must be determined by the differences in zero point energies of the various transition states for loss of H_2, HD, and D_2. This is again a strong indication that the reaction itself [Eq. (9)] is near thermoneutral, a situation which would maximize the isotope effect. Since the reaction is presumed to be slightly endothermic and being driven by the small amount of residual internal energy resulting from formation of the CH_3FD^+ ion then the relative zero point energies of the various isotopic transition states will play a determining role in the product distributions [35]. The ratio of H_2:HD:D_2 losses suggests that the transition state for H_2 loss lies ~0.7 kcal mol^{-1} below that for HD loss and ~1.3 kcal mol^{-1} below that for D_2 loss.

Finally, in the last type of experiment, CH_3F was pulsed into the FTICR cell containing a static pressure of CD_4. The data for this experiment, shown in Fig. 8, also gave $C_2H_3D_4^+$ as ~30% of the initial products and an initial ratio of H_2:HD loss of ~2:1. However, at longer reaction delays, the $C_2H_3D_4^+$ product represents ~50% of the C_2 products and the H_2:HD loss ratio is ~4:1. No loss of D_2 could be observed above the noise level, placing the H_2:D_2 loss ratio at >10:1. The rate constant in this case is again found to be 1.5×10^{-10} cm^3 molecule^{-1} s^{-1}. Due to the expense of CD_3F the analogous experiment using CD_3F in the

Table 2
Product distributions for the reaction of isotopic methylfluoronium ions with methane

Reaction		
$CH_3FD^+ + CD_4$	$\rightarrow C_2H_3D_2^+ + D_2 + DF$	0.04
	$\rightarrow C_2H_2D_3^+ + HD + DF$	0.18
	$\rightarrow C_2HD_4^+ + H_2 + DF$	0.46
	$\rightarrow C_2H_3D_4^+ + HF$	0.32
$CD_3FH^+ + CH_4$	$\rightarrow C_2H_4D^+ + D_2 + HF$	0.05
	$\rightarrow C_2H_3D_2^+ + HD + HF$	0.18
	$\rightarrow C_2H_2D_3^+ + H_2 + HF$	0.46
	$\rightarrow C_2H_4D_3^+ + HF$	0.31

pulsed valve and a static CH_4 pressure in the FTICR cell was not carried out.

The clustering data for $C_2H_7^+$ [13,14], accurate energetics for $C_2H_5^+$ and $C_2H_7^+$, and the product distributions and isotope effect data presented above provide the necessary input to construct a potential energy diagram for the $C_2H_7^+$ system. However, first some comment on the structures of the $C_2H_7^+$ ions implicated is in order. The two structures previously assumed were a C–C bond protonated ethane, I, and a classical ethyl cation bound to H_2, II [11,12]. However, while the calculated vibrational frequencies [22] for the more stable structure, I, were in good agreement with those experimentally observed by Yeh et al. [21] in the 2500–4000 cm^{-1} range, the vibrational frequencies [22] for the less stable form, II, differed considerably from the experimental values. Several years ago, on the basis of conventional ICR experiments on the $C_2H_7^+$ system, we had proposed that the first minimum encountered on the approach of a nonclassical $C_2H_5^+$ to H_2 would, logically, not be structure II, but rather a species, III, in which a nonclassical ethyl cation is bound to H_2 in a proton bound dimerlike structure [36]. This proposed structure is analogous to the bridged H_5^+ structure [37] and to a CH_3O^+ structure [38] which has been suggested to have the character of a protonated CO loosely bound to H_2. The most recent ab initio calculations [39] show that classical $C_2H_5^+$ is not a minimum on the potential energy surface. A species formally corresponding to this structure, lying ~7 kcal mol^{-1} above nonclassical $C_2H_5^+$, contains one negative frequency and thus likely corresponds to a transition

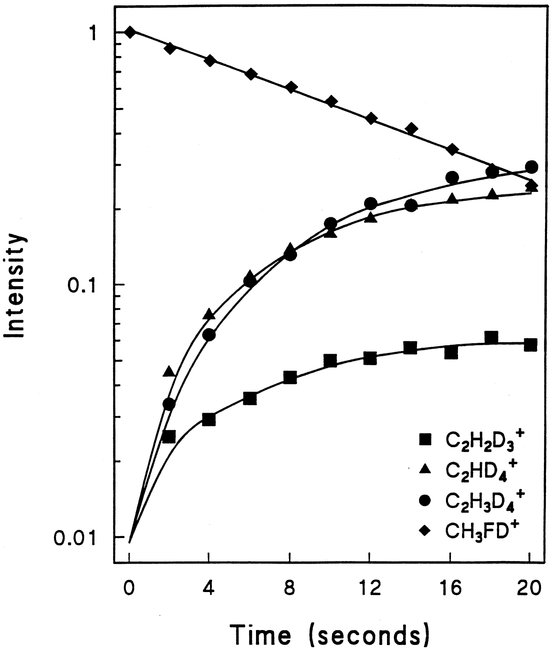
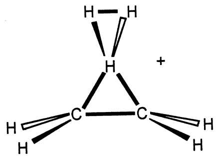
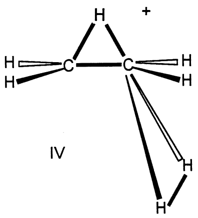


Fig. 8. Variation of relative ionic abundances as a function of time after isolation of CH_3FH^+ from a 1.5 ms. pulsed valve addition of CH_3F to CD_4 in the FTICR cell at a pressure of 1.5×10^{-9} Torr.

state for a hydrogen scrambling process in $C_2H_5^+$. It thus seemed highly unlikely to us that the nonclassical ethyl cation could rearrange at low temperature as a result of the interaction with H_2 to lead to II without any activation energy. The HPMS clustering experiments [13] found that a weakly bound species is easily formed, without an activation barrier, hence leading us to propose a species such as III as the low temperature cluster ion. In order to assess this conjecture ab initio calculations at very high levels of basis set including electron correlation for I, II, III, CH_3^+, CH_4, $C_2H_5^+$, and H_2 were carried out in order to provide a complete and reasonably accurate picture of the potential energy surface. However, while our calculations were underway, the analogous study by Carneiro et al. [17] appeared. These calculations were at a much higher level of theory than that possible in our laboratory and were successful in locating a structure such as III as a stable minimum, as well as another structure, IV, of comparable energy and which is also a feasible candidate for a species formed without activation energy when nonclassical $C_2H_5^+$ approaches H_2.

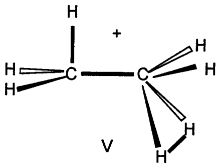


III



IV

The electronic energies showed that III and IV were bound by roughly 1 kcal mol^{-1}, however when zero point energy and thermal corrections were made this was reduced to almost no binding relative to separated $C_2H_5^+$ and H_2. As a result, these authors concluded that structures such as III and IV were not experimentally accessible and could then not be the low temperature species observed either in the HPMS experiments or the spectroscopic observations. Nevertheless, as noted above, the potential energy surface that these authors do recommend is not consistent with either of these experiments since it involves an entrance channel barrier of 2.9 kcal mol^{-1} between $C_2H_5^+ + H_2$ and II. Such a barrier would prevent the observation of II at low temperature in the HPMS experiments since there would be insufficient energy available to overcome this barrier. The nature of the transition state found V, closely resembles the opening up of nonclassical to classical ethyl cation, in either III or IV, to lead to II.



V

Further, the calculations find no barrier between I and II in excess of the energy of separated $C_2H_5^+$ and H_2. Again, if this were the case, II would never be observed experimentally as the approach of $C_2H_5^+$ to H_2 would provide sufficient energy for the system to pass directly from II to I. At best, an equilibrium mixture of I and II would be formed which, given the energetic difference between I and II, would contain virtually no II. Thus, the potential energy surface proposed by Carneiro et al. [17] is inconsistent with the HPMS experiments.

A consideration of the vibrational data of Yeh and co-workers [21] also leads to the conclusion that structures like III or IV correspond to the species exhibiting a vibration near 4000 cm^{-1}. These same authors had previously examined the trends in H_2 stretching frequency as a function of the bond energy in weakly bound $H(H_2)_n^+$ [40] and $H_3O^+(H_2O)_n(H_2)$ [41] clusters for which bond dissociation energies for loss of H_2 are experimentally known. On this basis they concluded that the bond energy to H_2 in $C_2H_7^+$ in the species exhibiting a vibrational frequency at 3964 cm^{-1} is ~4 kcal mol^{-1}, in excellent agreement with that found for the low temperature species found in the HPMS experiments. Structures such as III and IV, which have very short H–H distances are thus excellent candidates for such a frequency. While Carneiro et al. [17] do not report frequencies or entropies for III and IV, our own calculations gave an entropy change of −15 cal mol^{-1} K^{-1} for formation of III from

$C_2H_5^+ + H_2$ and a (scaled) frequency of 4036 cm^{-1} for the H–H stretch. These values are consistent with the fact that the calculated bond energy also underestimates the 4 kcal mol^{-1} experimentally observed, however the frequency is an excellent match for the vibrational observation of Yeh and co-workers [21]. Thus it appears likely that the ab initio calculations have underestimated the bond energy in I and III by roughly 2 and 4 kcal mol^{-1}, respectively. The latter is somewhat outside the range of "chemical accuracy" of 2.5 kcal mol^{-1} ascribed to G2 calculations but it is worth noting that at the same level of theory used by Carneiro et al. [17] the proton affinity of isobutene, which involves conventional structures, is overestimated by ~4 kcal mol^{-1}.

The ΔH° and ΔS° data from both experiment and theory allow us to propose the potential energy surface shown in Fig. 9 for the $C_2H_7^+$ system. As a result it appears highly unlikely that any experiments have resulted in production of an isolated, long lived classical form, II. Rather this species is simply a local minimum through which the system passes when III rearranges at high temperature to the most stable form, I, or when $C_2H_7^+$ formed at low pressure by the addition of CH_3^+ to CH_4 rearranges to lose H_2 via III. At best an equilibrium mixture of I and II may be generated at very high temperatures in a high pressure ion source.

Consideration of the position and structure of the transition state separating III from II and I may also permit an interpretation of the isotope effects reported in Table 2 based on the assumption that the transition state associated with H_2 loss will closely resemble separated $C_2H_5^+ + H_2$. Toward this end calculations were performed to obtain the zero point energy difference between the combinations of products found in Table 2. In excellent accord with the experimentally observed product distributions it was found that the most energetically favourable product combinations always maximize the number of hydrogens in the molecular dihydrogen lost.

Thus although some of the quantitative data obtained by ab initio calculations are not in perfect agreement with the experiments, the arguments advanced herein make it very likely that the $C_2H_7^+$ potential energy surface has the form described in Fig. 9.

4. Conclusion

Fourier transform ion cyclotron resonance experiments have been carried out which elucidate the details of the reaction of CH_3^+ with CH_4. Conclusive evidence is obtained to show that a $C_2H_7^+$ intermediate is involved in the formation of $C_2H_5^+$ and H_2 in this reaction. Under all pressure conditions of any mass spectrometric experiment the $C_2H_7^+$ formed has a lifetime that is too short to permit it to be collisionally stabilized. The $C_2H_7^+$ that has been observed at elevated ion source pressures in some mass spectrometric experiments is shown to very probably be the result of a reaction with a low level C_2H_6 impurity. Formation of the $C_2H_7^+$ intermediate by less energetic means, such as the transfer of CH_3^+ to CH_4 from CH_3FH^+, is shown to result in a very long lived species which very slowly eliminates H_2 to give $C_2H_5^+$. Examination of isotopic variants of this reaction show a dramatic deuterium isotope effect which is the result of a lower zero point energy for the transition state for elimination of H_2 relative to those for HD and D_2 elimination. In contrast to previous descriptions of the $C_2H_7^+$ potential energy surface it is proposed that the higher energy form of the ion experimentally observed has the structure of a nonclassical protonated ethylene which is bound to H_2 via the bridging hydrogen of the $C_2H_5^+$ unit rather than a classical $C_2H_5^+$ bound to H_2 via the carbocation center. Ab initio calculations [17] have been performed which support the existence of this new form of $C_2H_7^+$ and reveal that it is lower in energy that $C_2H_5^+ + H_2$. The calculated H–H stretching frequency in this new form of the ion is in excellent accord with that observed by Yeh and co-workers [21] in consequence spectroscopic experiments on $C_2H_7^+$. The enthalpy and entropy data derived from the ab initio calculations as well as data for the transition state separating I and II indicate that the classical form of the ion, II, likely does not exist as an isolated entity but rather only as a minor component in equilibrium

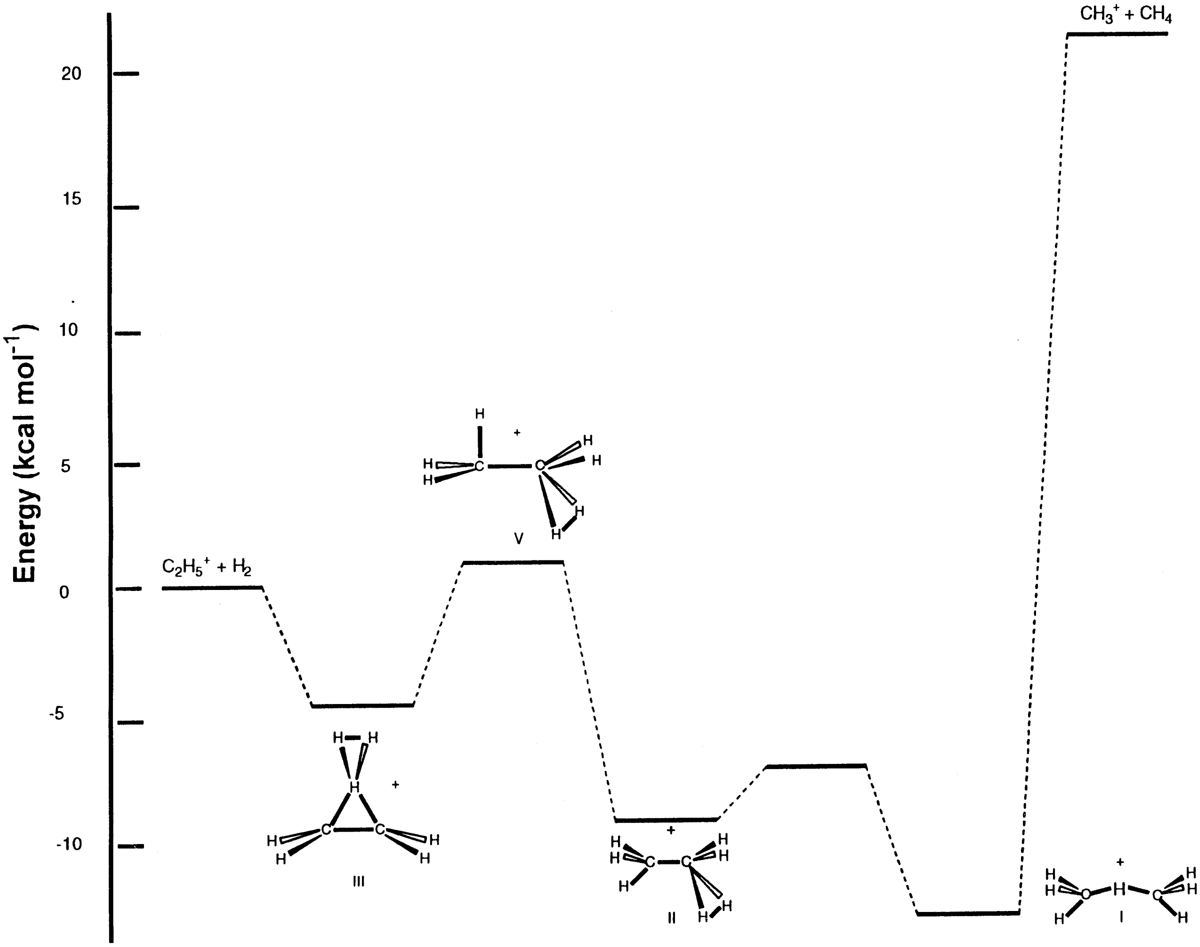


Fig. 9. Proposed potential energy diagram for the reaction of CH_3^+ and CH_3FH^+ with CH_4. The shaded area represents the approximate range of internal energies available to the initially formed CH_3FH^+.

mixtures with I. The ab initio calculated zero point energy difference between isotopic variants of the ethyl cation + hydrogen product arising from unimolecular dissociation of chemically activated $C_2H_7^+$ also serves to understand the dramatic isotope effect observed.

Acknowledgement

The generous financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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