Reversible Reactions of Gaseous Ions. III. Studies with Methane at 0.1–1.0 Torr and 77–300°K

F. H. Field[*1a] **and D. P. Beggs**[1b]

Contribution from the Corporate Research Laboratories,
Esso Research and Engineering Company, Linden, New Jersey 07036.
Received July 8, 1970

Abstract: The mass spectra of methane have been determined at temperatures between room temperature and liquid nitrogen temperature and pressures between 0.1 and 1.0 Torr. The following reactions are observed to take place: $CH_5^+ + CH_4 = C_2H_9^+$, $C_2H_5^+ + CH_4 = C_3H_9^+$, and $C_2H_9^+ + CH_4 = C_3H_{13}^+$. Collision-induced metastable ions corresponding to the reverse reactions in these equilibria are observed. The temperatures at which the reactions begin to occur to significant extents are different. At temperatures below about −150° the $C_2H_9^+$ (*m/e* 33) and $C_3H_9^+$ (*m/e* 45) ions are the dominant ions in the methane spectrum. Equilibrium constants for the above reactions are calculated, and from these values and their temperature coefficients, thermodynamic values for the reactions are obtained. The values of ΔG_{298} for the reactions above are −0.45, +0.16, and +0.69 kcal/mol, respectively. Thus the complexes are bound by weak forces, but it is suggested that they are chemical (as distinguished from physical) forces. Heats of formation of the new ions are 200, 199, and 181 kcal/mol, and the proton affinity of propane is calculated from the heat of formation of $C_3H_9^+$ to be 141 kcal/mol.

We have recently made a mass spectrometric study of the methane–water system over an extended range of temperature,[2] and in the course of this work interesting reactions were observed in methane alone at subambient temperatures. As a result, the investigation reported in this paper was undertaken. Specifically, we have determined the mass spectra of pure methane at temperatures between room temperature and liquid nitrogen temperature and pressures between 0.1 and 1.0 Torr.

The ion–molecule reactions occurring in methane at temperatures above ambient have been investigated by many workers, and we cite as representative examples a study carried out previously in this laboratory[3a] and the tandem mass spectrometer work of Abramson and Futrell.[3b] Cassuto[4] has investigated the reaction

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \qquad (1)$$

at temperatures down to −150°, and he finds that the rate constant for the reaction is effectively independent of temperature.

Experimental Section

These experiments were done with the Esso chemical physics mass spectrometer using the new ion source (source III) described previously.[2] This source is fabricated with a channel through which refrigerant can be passed, and temperatures down to −77°K can be achieved using liquid nitrogen as the refrigerant. For temperatures between liquid nitrogen temperature and ambient temperature cooled nitrogen gas is used as the refrigerant. A satisfactory degree of temperature control can be achieved by manual adjustment of the degree of cooling and/or the flow rate of the nitrogen gas. The temperature is measured by means of a chromel–alumel thermocouple attached to the block and to the cover plate of the ionization chamber. The standard voltage–temperature calibrations were used.

The question of the extent to which the reactant gas achieves temperature equilibrium with the walls of the ionization chamber has been considered in our earlier work concerned with temperature effects on chemical ionization mass spectrometry,[2,5] and we concluded that for ionization chamber temperatures above ambient temperature, equilibrium is achieved. We believe that the same arguments apply for the measurements with the new source for temperatures below ambient. In our previous work we showed[2] that above ambient temperature the ionization chamber pressure is a linear function of temperature for constant flow through the source, and we postulated that the linearity is evidence for the attainment of temperature equilibrium. We give in Figure 1 a plot of ionization chamber pressure as a function of subambient temperatures when the flow through the source is maintained constant by use of a Matheson subatmospheric pressure regulator. We believe that the linearity exhibited indicates that temperature equilibrium also is attained at low temperatures.

All of the measurements reported in this work were made under the so-called approximate field-free conditions,[2] which means that the ions in the ionization chamber and those just outside the ionization chamber are subjected to the weakest electric and magnetic fields compatible with a satisfactory sensitivity for detection of the ions by the mass spectrometer. A schematic drawing of the source has been given previously.[2]

In the subambient temperature range the minimum repeller voltage depends upon the temperature, for as the temperature of the source is lowered it is necessary to increase the repeller voltage to higher values to maintain satisfactory ion sensitivity. Typically we applied 2 V to the repeller at room temperature, but this was increased in a stepwise fashion to about 8 V as the temperature was decreased to its minimum value. No changes in the spectra or equilibrium constants seem to result from these changes in repeller voltage. The overall behavior of the machine under the approximate field-free conditions leads us to believe (although we certainly cannot offer unequivocal proof) that the positive ions are held in the ionization chamber by some sort of attractive force (perhaps the negative space charge of the electron beam), and the repeller field is necessary to overcome this attraction. Then the change in repeller field required by changes in temperature might well result from changes with temperature of the attractions acting upon the ions. If this be the case, the net force pushing the ions out of the ionization chamber may not be very much different in the measurements at different temperatures.

The methane used in the studies was Matheson Gold Label. The purity analysis is supplied by the manufacturer, and the only impurity of any significance for this work is C_2H_6, present to the extent of 35 ppm. We verified this figure by our own gc analysis. Propane concentration is given as <5 ppm. In addition, however, a trace quantity of water is present, and while the amount is small, it is sufficient to effect a partial consumption of the methane ions. Consequently, the methane introduced into the mass spectrometer

---

(1) (a) Address correspondence to this author at The Rockefeller University, New York, N. Y. 10021; (b) Esso Postdoctoral Fellow.

(2) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1567 (1971).

(3) (a) F. H. Field and M. S. B. Munson, *ibid.*, **87**, 3289 (1965); (b) F. P. Abramson and J. H. Futrell, *J. Chem. Phys.*, **45**, 1925 (1966); **46**, 3264 (1967).

(4) A. Cassuto, *Advan. Mass Spectrom.*, **2**, 296 (1963).

(5) F. H. Field, *J. Amer. Chem. Soc.*, **91**, 2827 (1969).

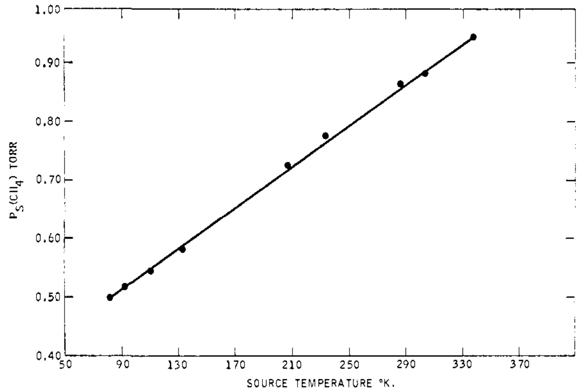

Figure 1. Methane source pressure *vs.* source temperature. Constant flow rate.

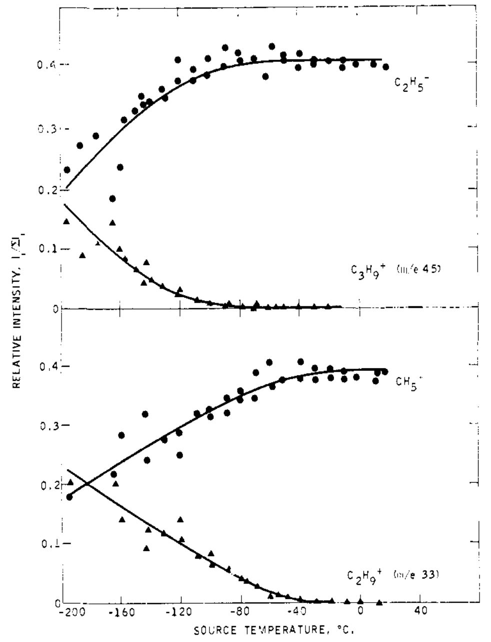

Figure 2. Relative intensities *vs.* source temperature for major methane ions; $P_s(CH_4) = 1.00 \pm 0.05$ Torr.

was passed through a glass spiral immersed in a 2-propanol-Dry Ice mixture maintained at a temperature of about −70°. Lower temperatures effected condensation of the methane. The procedure used reduce the water concentration to an acceptable low level.

Results and Discussion

Two different kinds of experiments were made: (1) studies wherein the ionization chamber temperature was varied at constant (±5%) pressure of methane, and (2) studies wherein the ionization chamber pressure of methane was varied at constant ionization chamber pressure. We will present the results of these temperature studies and pressure studies separately.

Temperature Studies. Methane spectra at P_s = 1.00 ± 0.05 Torr at three values of the ionization chamber temperature are given in Table I. In addition we give the spectrum of methane at 210° taken from our earlier work.[3a] In the table we include ions with relative intensities of 0.1% or greater. We give in Figure 2 plots of the trends with temperature of the intensities of the major ions in the methane spectrum, and in Figure 3 we give the trends of the minor ions. The data in Figures 2 and 3 are taken from three replicate determinations.

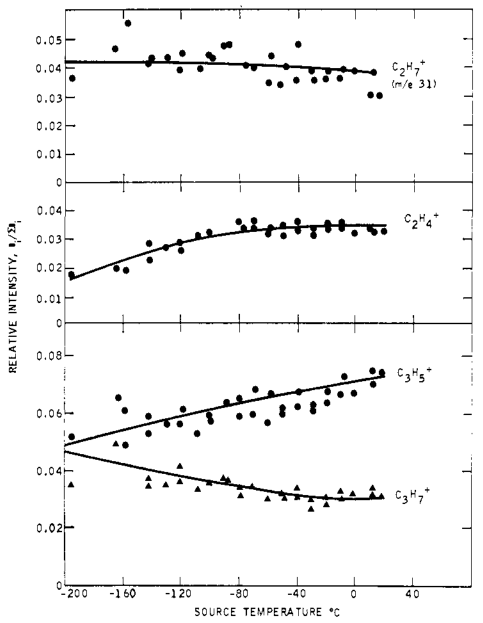

Figure 3. Relative intensities *vs.* source temperature for minor methane ions; $P_s(CH_4) = 1.00 \pm 0.05$ Torr.

The most interesting result shown in Table I and more clearly in Figure 2 is the fact that as the temperature is decreased, the relative intensity of the CH_5^+ ion begins to decrease at about −40°, and concomitantly an ion with *m/e* 33 appears and begins a monotonic increase. Similarly at about −80° the $C_2H_5^+$ intensity begins to decrease, and this decrease is matched by a monotonic increase in intensity of an ion with *m/e* 45. At the lowest temperatures studied these new ions with *m/e* 33 and 45 are major ions in the spectra. The diminution in the CH_5^+ intensity is approximately equaled by the increase in the *m/e* 33 intensity, and similarly the decrease in $C_2H_5^+$ intensity is approximately equaled by the increase in *m/e* 45 intensity. Although ions attributable to ^{13}C isotope contributions are not listed in Table I, in fact ions with *m/e* 34 and 46 are observed. A calculation based on a representative number of experimental points gives the result that on the average the *m/e* 34 intensity is 2.7% of the *m/e* 33 intensity, and the *m/e* 46 intensity is 3.9% of the *m/e* 44 intensity. We consider that allowing for experimental error these percentages

Table I. CH_4 Mass Spectra at Various Temperatures[a,b]

		Relative intensity, $I_i/\Sigma I_i$			
m/e	Ion	210°[c]	11°	−80°	−195°
17	CH_5^+	0.478	0.385	0.357	0.178
28	$C_2H_4^+$	0.020	0.0324	0.0346	0.0162
29	$C_2H_5^+$	0.406	0.403	0.421	0.234
31	$C_2H_7^+$	0.0012	0.0305	0.0472	0.0353
33	$C_2H_9^+$	0	0.0013	0.0405	0.203
41	$C_3H_5^+$	0.055	0.0688	0.0637	0.0507
43	$C_3H_7^+$	0.0071	0.0313	0.0335	0.0349
45	$C_3H_9^+$	0	0.0008	0.0037	0.149
49	$C_3H_{13}^+$	0	0	0.0006	0.0318
57	$C_4H_9^+$	0.0013	0.0100	0.0084	0.0028
60	?	0	0	0	0.0132

[a] $P_s(CH_4) = 1.00 \pm 0.05$ Torr. [b] Ions due to ^{13}C content omitted from tabulation. [c] From ref 3a; $P_s(CH_4) = 0.91$ Torr.

indicate the presence of two carbon atoms in the *m/e* 33 ion and three carbon atoms in the *m/e* 45 ion. One can conceive of the possibility that ions with these masses might be oxygen-containing ions, for example, HOO^+ for *m/e* 33 and $C_2H_5O^+$ or $HCOO^+$ for *m/e* 45. However, it must be remembered that these ions are observed down to liquid nitrogen temperature, and our observation has been that oxygenated compounds such as water or alcohols introduced into the mass spectrometer freeze out at this temperature and do not produce a signal. Carbon dioxide is perhaps borderline in this regard, but no significant amount of protonated carbon dioxide is observed in our system at any temperature. Molecular oxygen will not be condensed at liquid nitrogen temperature, but we have shown[6] that the ions from methane do not react with molecular oxygen at elevated temperatures, and no compelling reason exists to think that the behavior will be different at low temperatures. Furthermore, to the best of our knowledge the methane used in this investigation did not contain significant amounts of carbon dioxide and oxygen.

Taking into account all of the evidence we postulate that the *m/e* 33 ion has the formula $C_2H_9^+$ and that the *m/e* 45 ion has the formula $C_3H_9^+$. From the fact that the temperature at which CH_5^+ begins to decline equals that at which $C_2H_9^+$ first appears, we postulate that $C_2H_9^+$ is formed from CH_5^+ by the reaction

$$CH_5^+ + CH_4 \rightleftarrows C_2H_9^+ \qquad (2)$$

and from a similar temperature equality for $C_2H_5^+$ and $C_3H_9^+$ we postulate the occurrence of the reaction

$$C_2H_5^+ + CH_4 \rightleftarrows C_3H_9^+ \qquad (3)$$

Reactions 2 and 3 are written as equilibrium reactions, and this will be discussed later. In reactions 2 and 3 the product ions are written as $C_2H_9^+$ and $C_3H_9^+$, respectively, but they also can be written as $CH_5^+ \cdot CH_4$ and $C_2H_5^+ \cdot CH_4$.

Another interesting feature of the methane spectrum is the fact that at the lowest temperatures studied one observes the growth of an ion with *m/e* 49. It achieves a relative intensity of 0.0318 at −195°, and this figure is entered in Table I, but it is inconvenient to attempt to represent the intensities of this ion graphically. The intensities are too small to obtain reliable ^{13}C isotope ion intensities, and they are also too small to affect significantly the intensity of any possible reactant ion. Thus more uncertainty exists concerning this ion than those discussed above, but we feel reasonably confident in postulating that *m/e* 49 is a hydrocarbon ion, in which case its formula is $C_3H_{13}^+$. This can also be written as $CH_5^+ \cdot (CH_4)_2$. We suggest that the reaction by which this ion is formed is

$$CH_5^+ \cdot CH_4 + CH_4 \rightleftarrows CH_5^+ \cdot (CH_4)_2 \qquad (4)$$

At the lowest temperatures studied ions with *m/e* values of 58, 59, 60, and 61 are observed with low intensities. Only one of these (*m/e* 60) becomes large enough to warrant inclusion in Table I. Again, we consider it likely that it is a hydrocarbon ion, in which case its formula would be $C_4H_{12}^+$, but we are unable to guess at the reaction which forms it.

We consider now other features of Table I and Figure 3. The agreement between the methane spectrum obtained in 1965 at 210° [3a] and the spectrum at 11° obtained in the present work is reasonably satisfactory. We are unable to advance a meaningful explanation for the difference in the relative intensities found for CH_5^+ ion. The intensity for *m/e* 31 is roughly 30 times higher in the present experiments than in the 1965 experiments. One sees from Figure 3 that the relative intensity of this ion is essentially invariant over the whole temperature range investigated. We suggested earlier[3a] that $C_2H_7^+$ in methane is formed primarily by proton transfer to ethane impurity and that the formation of $C_2H_7^+$ in methane alone by the three-body process

$$CH_3^+ + CH_4 \longrightarrow (C_2H_7^{+*}) \xrightarrow{CH_4} C_2H_7^+ + CH_4 \qquad (5)$$

is probably quite small. More recently, Wolfgang and coworkers[7] find that the formation of $C_2H_5^+$ from CH_3^+ and CH_4 proceeds by a direct mechanism and that the probable reason for this behavior is that the activation energy for decomposition of $C_2H_7^+$ may be as low as 0.1 eV. Our new results support this point of view. The ethane content in the methane used in this work was higher than that used in our 1965 study, and this accounts for the higher intensity of *m/e* 31 observed in the present work. Lowering the temperature does not effect enough stabilization of the intermediate complex written in reaction 5 for the intensity of this ion to rise above the $C_2H_7^+$ intensity produced from ethane. It is also worthy of note that the constancy of the $C_2H_7^+$ intensity shown in Figure 3 constitutes evidence that in the temperature range studied $C_2H_7^+$ does not react further with methane. We reject as unlikely the possibility that the observed constancy is the consequence of compensating effects, namely, increased stabilization of $C_2H_7^{+*}$ and increased reactivity of $C_2H_7^+$ as the temperature decreases.

The $C_3H_7^+$ intensity (*m/e* 43) is higher in the current work than in the 1965 work. As the temperature decreases the intensity of $C_3H_7^+$ increases somewhat, and at the same time the intensity of $C_3H_5^+$ decreases somewhat (Figure 3). The larger intensity of $C_3H_7^+$ in the current work may result from a higher propane impurity in the methane, although the propane content is small (less than 5 ppm). On the other hand, the trends with temperature observed in the $C_3H_7^+$ and the $C_3H_5^+$ intensities are compatible with the stabilization of an intermediate complex, and we suggest the possibility that in the reactions

$$\begin{array}{llr} C_2H_3^+ + CH_4 \longrightarrow (C_3H_7^{+*}) \xrightarrow{CH_4} & \underset{m/e\ 43}{C_3H_7^+} & (6a) \\ \qquad\qquad\qquad\qquad\quad \llcorner\!\!\longrightarrow & \underset{m/e\ 41}{C_3H_5^+} + H_2 & (6b) \end{array}$$

the stabilization involved in (6a) occurs to an increased extent at lower temperatures. Beyond this, the $C_3H_7^+$ and $C_3H_5^+$ plots suggest that no significant further reaction of either of these ions with methane is occurring at low temperatures.

The decline in the $C_2H_4^+$ intensity (Figure 3) suggests that some reaction with methane is occurring as the temperature is lowered, but the decline is a gentle one

---

[6] M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, 87, 4242 (1965).

[7] Z. Herman, P. Hierl, A. Lee, and R. Wolfgang, *J. Chem. Phys.*, 51, 454 (1969); see also R. Wolfgang, *Accounts Chem. Res.*, 3, 48 (1970).

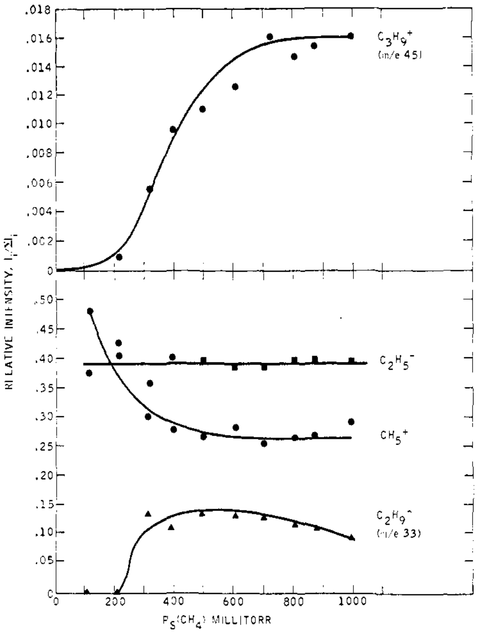

Figure 4. Relative intensities *vs.* source pressure for major methane ions; temp$_s$ = −110°.

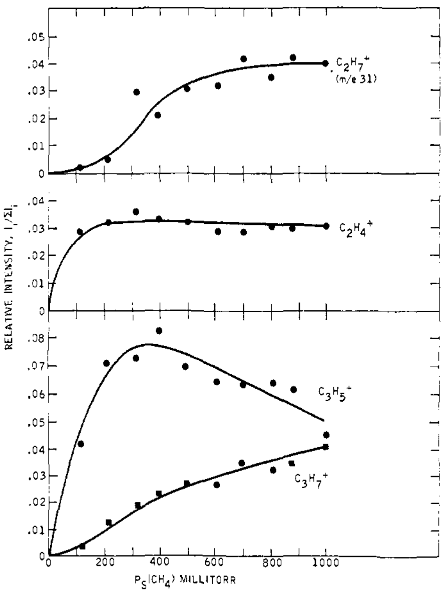

Figure 5. Relative intensities *vs.* source pressure for minor methane ions; temp$_s$ = −110°.

and the initial intensity is small, and no further speculations are possible.

Temperature runs similar to those shown in Figures 2 and 3 were also made at methane source pressures of about 0.5 and 0.115 ± 0.025 Torr. The results at about 0.5 Torr are not significantly different from those given in Figures 2 and 3, and they will not be given. At 0.115 Torr no significant change in the relative intensities of CH_5^+, $C_2H_5^+$, and $C_2H_4^+$ occur over the temperature range investigated (+4 to −165°), and thus the rate constants for the formation of these ions are temperature independent. This is in agreement with the finding for CH_5^+ made by Cassuto.[4] The relative intensity of the CH_5^+ ion is higher than that found in the present work at a source pressure of 1 Torr. We shall see later that a higher relative intensity is consistently observed for this ion at low pressures, and we do not think the effect results from experimental error. However, we do not understand what is happening.

Pressure Studies. These studies involved measuring the mass spectra of methane at several different values of the pressure of methane in the ionization chamber at constant temperature. The temperatures were −110 and −50°. The results at the two temperatures do not differ in unexpected ways, and only the results at −110° are given (Figures 4 and 5). The intensity of CH_5^+ is 48% of the total ionization at a pressure of 0.115 Torr, and it exhibits a sharp initial decrease as the pressure is increased. Between 0.2 and 0.3 Torr, $C_2H_9^+$ exhibits a sharp increase, which accounts for much, but not all, of the initial decrease in CH_5^+. While some experimental uncertainty exists, it appears from Figure 4 that an unaccountable decrease in CH_5^+ occurs between 0.1 and 0.2 Torr. By contrast the intensity of $C_2H_5^+$ is constant within experimental error. We have postulated that $C_3H_9^+$ is formed from $C_2H_5^+$ by reaction 3, but at the temperature of −110° the amount of $C_3H_9^+$ formed is small enough that the corresponding diminution in $C_2H_5^+$ is obscured by experimental uncertainty. The question of the quantitative relationship between the intensities of $C_2H_9^+$ and CH_5^+ and between $C_3H_9^+$ and $C_2H_5^+$ will be discussed later.

One observes from Figure 5 that the intensity of $C_2H_4^+$ rises sharply from the origin, and this behavior is in accordance with the known[3a] formation of $C_2H_4^+$ by a process which is second order in methane pressure. The intensity of $C_3H_5^+$ rises sharply (although not so sharply as that of $C_2H_4^+$) and then shows a gentle decline. The pressure dependence of $C_3H_7^+$ is obviously of a higher order than that of $C_3H_5^+$. The behavior is in accordance with the known[3a] third-order dependence of $C_3H_5^+$ intensity, and the relationship between $C_3H_5^+$ and $C_3H_7^+$ is in accordance with the postulate made earlier that $C_3H_7^+$ is produced by reaction 6a (fourth order in CH_4 pressure) and $C_3H_5^+$ is produced by (6b). The pressure dependence for the formation of $C_2H_7^+$ appears to be similar to that for $C_3H_7^+$, which is compatible with the formation of the ion by the protonation of ethane by CH_5^+, but with the added necessity of an additional collision with a molecule of methane to stabilize the $C_2H_7^{+*}$ initially formed. It is not so compatible with a postulate of the formation of the ion by reaction 5.

Metastable Ions. The methane spectra contain diffuse, metastable-like peaks, and the intensities of these depend upon the source pressure of methane and the source temperature. In Table II we summarize

Table II. Metastable Ions in Methane

*m/e**, obsd	Temp range,[a] °C	Postulated process	*m/e**, calcd	Comment
8.8	<−50	$C_2H_9^+ \rightarrow CH_5^+ + CH_4$	8.75	Very sharp peak
18.7	<−100	$C_3H_9^+ \rightarrow C_2H_5^+ + CH_4$	18.7	Very sharp peak
22.3	<−150	$C_3H_{13}^+ \rightarrow C_2H_9^+ + CH_4$	22.2	Very sharp peak
25.1	All	$C_2H_5^+ \rightarrow C_2H_3^+ + H_2$	25.1	Diffuse peak
27.1	All	$C_2H_7^+ \rightarrow C_2H_5^+ + H_2$	27.1	Diffuse peak

[a] Source temperature below which metastable ion is observed.

the observations made. The intensity of the metastable ion with apparent *m/e* 8.8 is large enough at −110° that it was possible to observe the effect of pressure on the intensity. A plot of the ratio of the peak height of the ion at *m/e* 8.8 to that of the ion at *m/e* 33 as a function of pressure was constructed, and it was found to be a monotonically increasing function passing through the origin. Thus the metastable ion at *m/e* 8.8 is a collision-induced ion rather than a spontaneous metastable. A similar plot was made of the ratios of intensities of *m/e* 25.1 to those of *m/e* 29, and this plot also increased with pressure and passed through the origin. However, the intensity at P_s = 1.0 Torr was only about one-tenth that of the *m/e* 8.8 ion. It also is a collision-induced ion, and we conclude that in general the diffuse, "metastable" ions observed in the spectra have an appreciable collision-induced component. Indeed, it may well be that these ions are all collision induced.

Nevertheless, we are inclined to believe that they provide the same kind of information concerning decomposition paths of ions as do the spontaneous metastable ions in conventional electron-impact spectra. For the collision-induced ion to be collected in the mass spectrometer, it cannot suffer a significant deflection of its path, and under these circumstances the collision can be looked upon as a kind of Franck–Condon perturbation of the moving ion by the stationary neutral molecule with which it is interacting. Decompositions resulting from this perturbation will probably occur along established pathways and provide information about the identities of the pathways. According to this point of view, the ions at *m/e* 8.8, 18.7, and 22.3 constitute excellent evidence for the occurrence of the reverse reactions in (2), (3), and (4).

Quantitative Considerations. As we showed previously, the reactions producing $C_2H_9^+$ and $C_3H_9^+$ show strong negative temperature coefficients. Similarly, reaction 4 producing the $C_3H_{13}^+$ (*m/e* 49) ion also has a strong negative temperature coefficient, although it is not convenient to represent this graphically in Figure 2 or 3. All three of these reactions are association reactions, and it may be seen from the pressure studies depicted in Figure 5 that the intensities of $C_2H_9^+$ and $C_3H_9^+$ exhibit a high-order dependence on the methane pressure. Association reactions with a negative temperature coefficient and a high-order pressure dependence may constitute a kinetically limited termolecular reaction system, or, if sufficient time exists or a sufficient number of collisions are available, they may constitute systems in which thermodynamic equilibrium has actually been established.

In previously published works wherein association ions with negative temperature coefficients were observed,[2,8-10] we have represented the phenomena in terms of the equilibrium formulation. A recent careful investigation[2,10] of the water reversible reaction system in our mass spectrometer has shown that while some unresolved problems in this mode of representation exist, the weight of evidence indicates that under certain circumstances the association reactions achieve equilibrium in the mass spectrometer ionization chamber. We postulate that the present low-temperature methane results can also be represented in terms of the equilibrium formulation.

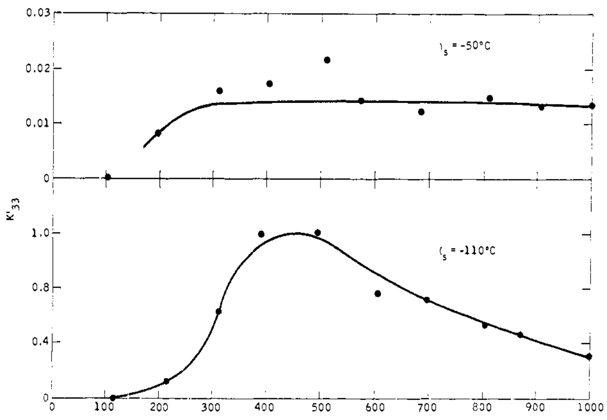

Figure 6. Equilibrium constants K' for $CH_5^+ + CH_4 \rightleftarrows C_2H_9^+$ as a function of $P_s(CH_4)$ at two source temperatures; standard state for K' is 1 Torr.

The two most important criteria for the establishment of equilibrium are: (1) the equilibrium condition be attained starting from either side of the reaction, and (2) the equilibrium constant be invariant over an appropriately wide range of variation of the concentrations of the components of the reaction. A criterion which is perhaps subsidiary to these two, but still of significance, is that the temperature variation of the equilibrium constant follow the van't Hoff relationship. Unfortunately, we are unable to utilize the criterion of approaching equilibrium from both directions for reactions 3, 4, and 5. Achieving this goal will require a considerable degree of ingenuity. We can investigate the second criterion by varying the methane pressure and observing the degree of constancy of the equilibrium constants. However, the range over which the pressure can be varied is limited at both ends. Below some minimum pressure the reactions occurring will of necessity be insufficient to establish equilibrium, and the upper limit is imposed by the pressure operating range of the mass spectrometer.

We give in Figure 6 equilibrium constants for reaction 2 as a function of source pressure of methane at two temperatures. The standard state for the equilibrium constants represented in the figure is 1 Torr. For reaction 2 the expression for the equilibrium constant is

$$K_P = (I_{33}/I_{17})(1/P_s(CH_4)) \qquad (7)$$

and analogously for reactions 3 and 4.

One observes different behavior at the two temperatures; namely, at the lower temperature the equilibrium constant passes through a maximum and then exhibits a steady decrease. At the higher temperature the equilibrium temperature rises from zero and remains sensibly constant between 300 and 1000 mTorr. Behavior of this sort has been observed and discussed in some detail previously.[2,10] It has been our observation that in our experiments equilibrium conditions are not obtained when the experimental conditions lead to the conversion of significant amounts of reactants to products. In general, difficulties are encountered when the product concentration becomes 10–20% of the reactant concentration, and the value of K_{33}' given in Figure 6 at −110° and P_s = 500 mTorr corresponds to

---

(8) F. H. Field, P. Hamlet, and W. F. Libby, *J. Amer. Chem. Soc.*, **91**, 2839 (1969).

(9) F. H. Field, *ibid.*, **91**, 6334 (1969).

(10) D. P. Beggs and F. H. Field, *ibid.*, **93**, 1576 (1971).

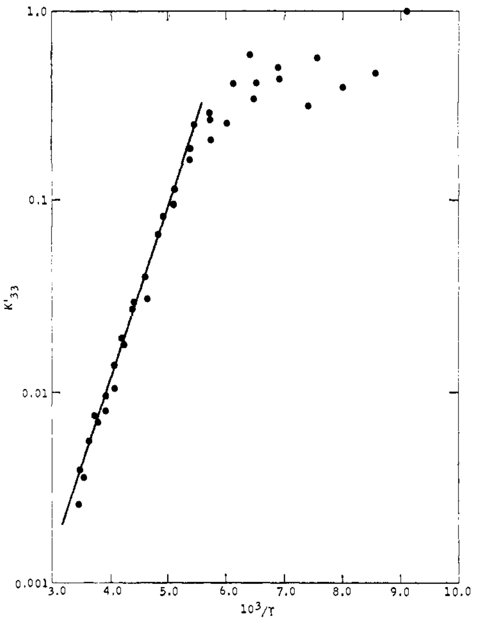

Figure 7. van't Hoff plot for $CH_5^+ + CH_4 \rightleftarrows C_2H_9^+$; standard state for $K' = 1$ Torr; $P_s(CH_4) = 1.0$ Torr.

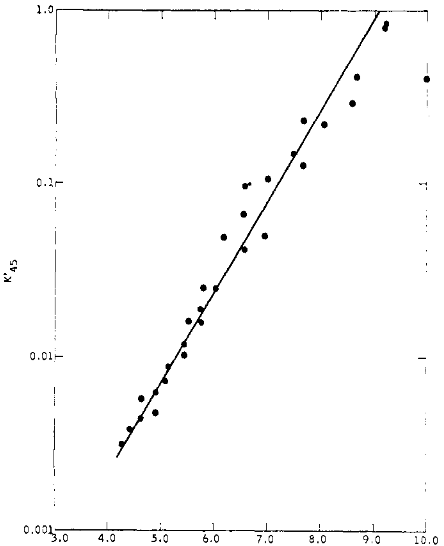

Figure 8. van't Hoff plot for $C_2H_5^+ + CH_4 \rightleftarrows C_3H_9^+$; standard state for $K' = 1$ Torr; $P_s(CH_4) = 1.0$ Torr.

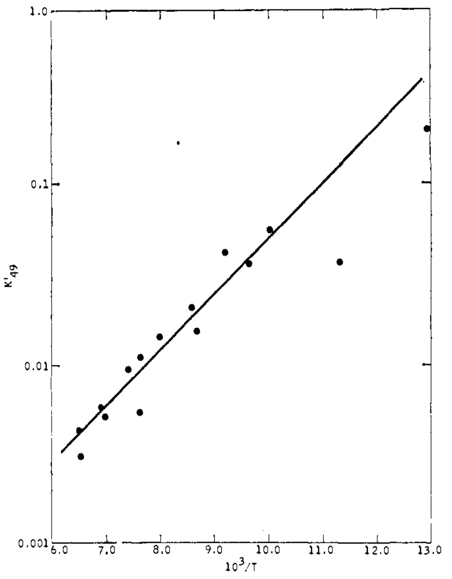

Figure 9. van't Hoff plot for $C_2H_9^+ + CH_4 \rightleftarrows C_3H_{13}^+$; standard state for $K' = 1$ Torr; $P_s(CH_4) = 1.0$ Torr.

a value of I_{33}/I_{17} of 0.5. On the other hand, in the experiment at −50°, the value of this ratio at $P_s = 1000$ mTorr is only approximately 0.01. We suggest that the decline in K_{33}' observed at the lower temperature above $P_s = 500$ mTorr is the result of time limitation on the establishment of sequential equilibria as described previously.[10] Under conditions where equilibrium constant values are constant with respect to pressure, linear van't Hoff plots are found for the temperature variation of equilibrium constants. By contrast, when the conditions are such that the equilibrium constant declines with pressure, deviations from linearity of the van't Hoff plots are observed. We believe that equilibrium is attained under conditions producing equilibrium constants independent of pressure and van't Hoff plots which are linear.

The plot of K_{45}' for reaction 3 as a function of methane source pressure at −110° was constant within limits of ±20% in the pressure range 300–1000 mTorr. The value of I_{45}/I_{29} was of the order of 0.05, and we consider the value of K_{45}' to be essentially independent of pressure. The values of K_{45}' in the pressure run at −50° was so small that a reliable plot could not be obtained. The values of K_{49}' for reaction 4 at −110° were within experimental error constant in the pressure range 300–1000 mTorr.

The van't Hoff plots obtained for reactions 2, 3, and 4 are given in Figures 7, 8, and 9, respectively. The points plotted are taken from replicate runs made on three different days. The plot for reaction 2 given in Figure 7 illustrates the phenomenon usually encountered; namely, at low amounts of reaction the van't Hoff plot is linear, but at lower temperatures and larger amounts of reaction the plot bends over and the slope becomes smaller. An explanation for the phenomenon in terms of time limitation on the establishment of equilibrium has been given previously.[10]

The plot for K_{45}' corresponding to reaction 3 is given in Figure 8. Comparing the K_{45}' values given in Figure 8 with the K_{33}' values given in Figure 7, both slopes and absolute magnitudes of the quantities given in the van't Hoff plots are compatible with the more qualitative observations demonstrated in Figure 2; namely, $C_2H_9^+$ is formed more readily and at a higher temperature than $C_3H_9^+$. The van't Hoff plot for K_{49}' corresponding to reaction 4 is given in Figure 9. The absolute intensities of the m/e 49 ion never become very large, and probably as a consequence of this the experimental scatter in Figure 9 is larger than in the other two van't Hoff plots.

We have calculated thermodynamic quantities from the linear portions of the plots in Figures 7–9, and these are given in Table III. The differences between the thermodynamic quantities for the different reactions are meaningful and are reflected in the easily observed differences in behavior described above. The trend in the enthalpies of reaction in proceeding from $C_2H_9^+$ to $C_3H_{13}^+$ is in accordance with the decreasing order of stability of these ions. The entropy changes seem to differ somewhat, but like many of the entropy change values that we have obtained for ions in our labora-

Table III. Thermodynamic Quantities for Three Equilibrium Reactions

Reaction	ΔH, kcal/mol	ΔS, cal/(deg mol)	ΔG_{298}, kcal/mol	K_{298}[a]
$CH_5^+ + CH_4 \rightleftarrows C_2H_9^+$	−4.14	−12.4	−0.45	2.13
$C_2H_5^+ + CH_4 \rightleftarrows C_3H_9^+$	−2.39	−8.6	+0.16	0.76
$C_2H_9^+ + CH_4 \rightleftarrows C_3H_{13}^+$	−1.47	−7.2	+0.69	0.32

[a] Standard state = 1 atm.

tory,[5,9] they are not as negative as one would expect for association reactions.

The ions $C_2H_9^+$ and $C_3H_{13}^+$ deviate so far from conventional ideas about valence that it is pointless to speculate about their structure, although obviously they are of much interest in this regard. The $C_3H_9^+$ ion has the same formula as protonated propane, and this ion has long been suspected to have at least a transitory existence,[11] although no convincing evidence for its existence as a stable entity has previously been available. It is possible that all three of these unusual ions are complexes held together by unspecific physical forces such as ion–induced dipole interactions. However, in fact it appears that an appreciable degree of specificity exists in the interactions observed. Thus, significant differences in the enthalpies and free energies of reactions 2 and 3 are observed. In addition, as was pointed out in the discussion of the data presented in Figure 3, not all of the ions produced in the methane spectrum at higher temperatures react at the lower temperatures to form complexes with methane. Specifically, the intensity of $C_2H_7^+$ seems to be quite invariant with temperature, and while we think that temperature affects the relative intensities of the $C_3H_7^+$ and $C_3H_5^+$ ions, the trends of their intensities give no indication of the formation of complexes with methane. On the other hand, some consumption of $C_2H_4^+$ seems to occur, although we have not been able to identify the product formed. On the whole, we believe that the weight of the evidence is that the bonding occurring in $C_2H_9^+$, $C_3H_9^+$, and $C_3H_{13}^+$ is more of a chemical than a physical nature.

If this be the case, it is of interest to calculate energetic quantities for these new ionic species. We use the enthalpy changes listed in Table III and heats of formation tabulated by Franklin, *et al.*[12] For the heat of formation of $C_3H_9^+$ formed by reaction 3 we calculate a value of 199 kcal/mol. If one assumes that the $C_3H_9^+$ formed in this reaction has the structure of protonated propane, this heat of formation corresponds to a proton affinity of propane of 141 kcal/mol. The proton affinity of methane may be calculated from the results of Munson and Field[11] and new values of ion energies[12] to be 122 ± 1 kcal/mol. Munson and Field showed that the proton affinity of ethane is greater than that of methane, and in turn that of propane is greater than that of ethane, and thus the value for the proton affinity of propane calculated here is reasonable. We call attention to the fact that with a value of $\Delta H_f(C_3H_9^+) = 199$ kcal/mol

$$C_3H_9^+ \longrightarrow sec\text{-}C_3H_7^+ + H_2 \qquad (8)$$

reaction 8 is 9 kcal/mol exothermic, taking the published value of 190 kcal/mol for the heat of formation of *sec*-$C_3H_7^+$. In the temperature range for which we observe the existence of $C_3H_9^+$, reaction 8 cannot occur to any significant extent, presumably because of the existence of an activation energy barrier of some sort. The heats of formation of $C_2H_9^+$ and $C_3H_{13}^+$ are calculated to be 200 and 181 kcal/mol, respectively. For these ions no exothermic decomposition paths exist.

Acknowledgment. D. P. Beggs wishes to express his appreciation to the Esso Research and Engineering Company for a postdoctoral fellowship which he held during the time when this work was done. We also wish to thank W. A. Petersen and T. M. Pugel for their assistance in carrying out these experiments.

---

(11) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965).

(12) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26** (1969).