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Reactions of Gaseous Ions. XIV. Mass Spectrometric Studies of Methane at Pressures to 2 Torr

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Gaseous ionic reactions have been observed in the source of a mass spectrometer at pressures as high as 2 torr. The general pattern of reactions is the same as that observed previously at pressures up to 0.3 torr. CH_3^+ , C_2H_4^+ , C_2H_5^+ , and C_3H_5^+ do not react appreciably with methane even though exothermic reactions can be written for the latter three ions. The rate constant for reaction of C_2H_2^+ with CH_4 is five times the rate constant for reaction of C_2H_3^+ with CH_4 . These observations of chemical effects on reaction rates are not explained by present theory. These data support the suggestions that the high molecular weight polymers formed in high energy irradiation of methane by ionic processes come from reactions of the hydrogen-deficient ions of low concentration, C^+ and CH^+ .

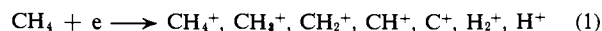
The gaseous ionic reactions occurring in methane have been investigated by numerous workers.¹⁻⁸ The trend in these studies has been to work at higher and higher source pressures, and as the source pressure is increased the degree of complexity of the reactions occurring and the extent of knowledge about ionic reactions have increased also. As a continuation of

this trend, we wish here to report our study on the ionic reactions in methane at pressures up to 2 torr in the source of the mass spectrometer.

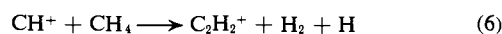
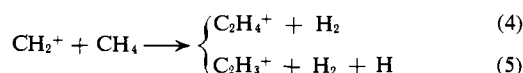
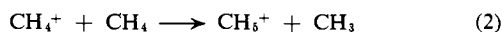
The most recently published studies report measurements at source pressures up to about 0.3 torr, and, making reasonable assumptions about the cross section and the mass spectrometer ionization chamber dimensions, one calculates that an ion formed in the electron beam will make 5-10 collisions with gas molecules in traversing the distance between the electron beam and the ion exit slit. If the pressure in the source is increased to 2 torr, the number of collisions made by an ion within the reaction chamber increases correspondingly to 30-70, and one approaches more closely than previously to macroscopic conditions. One can expect to observe high-order reactions, slow reactions, and reactions of ions with impurities or small amounts of added substances. We shall report reactions of ions from methane with added substances in subsequent papers.

On the basis of the studies made at source pressures up to 0.3 torr, it is generally agreed that the following are the most important ionic reactions occurring in methane.

Primary ions



Secondary reactions



(1) V. L. Tal'roze and A. L. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 909 (1952).

(2) (a) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); (b) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

(3) F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(4) V. L. Tal'roze and E. L. Frankevich, *Russ. J. Phys. Chem.*, **34**, 1275 (1960).

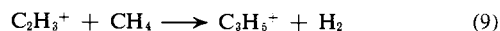
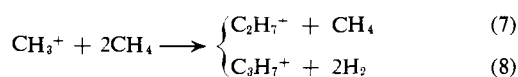
(5) R. Fuchs, *Z. Naturforsch.*, **16a**, 1026 (1961).

(6) S. Wexler and N. Jesse, *J. Am. Chem. Soc.*, **84**, 3425 (1962).

(7) F. H. Field, J. L. Franklin, and M. S. B. Munson, *ibid.*, **85**, 3575 (1963).

(8) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Chem. Phys.*, **40**, 5 (1964).

Tertiary reactions



Product ions of mass higher than that of C_3H_7^+ are found in the methane mass spectrum, but a difference of opinion^{6,7} exists as to whether the ions observed are truly formed as a result of gaseous ionic reactions with methane. The relative concentrations of the various ions formed at several pressures are given in Table I, which will be discussed later.

Experimental

The experiments were made with the Esso (formerly Humble) chemical physics mass spectrometer, which has previously been described.^{7,9} Two modifications were made for the measurements reported here. The more important is that the openings in the ionization chamber are made smaller to decrease gas flow and thus permit the experiments to be done at higher pressures. The new dimensions of the electron entrance slit are 0.05×3 mm., and those of the ion exit slit are 0.05×5 mm. The dimensions of the analyzer entrance slit are 0.25×10 mm., and an attempt to use a very narrow slit (0.05×10 mm.) to maintain a low analyzer pressure was unsuccessful. The differential pumping in the system is such that at a source pressure of 2 torr, the analyzer pressure is about 2×10^{-5} torr.

The other modification made in the equipment comprises an improvement in the method of measuring the pressure in the ionization chamber. A 4-mm. o.d. glass tube has been inserted down the inside of the gas entrance tube, and the end of this tube reaches to a point just behind the ion repellers in the ionization chamber. The other end of the tube passes out of the inlet line through a ring seal and is connected to a McLeod gauge. Thus the McLeod gauge measures the pressure in the ionization chamber directly. Direct measurement of the source pressure has been achieved previously.¹⁰ Checks were made between the pressures determined by the previously utilized thermistor technique⁹ and the pressures determined directly with the McLeod gauge. Excellent agreement (on the order of 1–2%) was found between the pressures determined by the two methods.

The ionizing electron current was about $0.05 \mu\text{a}$. measured with no gas in the ionization chamber. The electron current emitted from the Ir filament was maintained constant during each experiment. To improve the penetration of the electrons into the ionization chamber at high pressure, the electron voltage was maintained at 150 v. in the course of these measurements. The repeller voltage was maintained at 2.5 v. (6.25 v./cm.), and the ion-accelerating voltage was maintained at 3000 v. All measurements here reported were made with the metastable suppressor maintained at a high enough potential to suppress completely the

collection of collision-induced metastable ions. The source temperature was maintained at $210 \pm 10^\circ$.

It was found that the distribution of ions to be found in methane at high pressure depends very strongly on the presence of even quite small amounts of certain impurities (especially water and ethane), and special precautions had to be taken to ensure that reproducible, meaningful results were obtained. To try to understand early unreproducible results, a systematic variation of instrumental parameters was made which gave essentially no changes in the ionic distribution.

An appropriate amount of Phillips research grade methane was condensed in a trap with liquid nitrogen, and then a center cut was distilled onto Linde 5A molecular sieve maintained at liquid nitrogen temperature. A center cut was distilled from the material sorbed on the molecular sieve and stored in an appropriate glass vessel. The apparatus, including the molecular sieve, was evacuated for 12 hr. prior to use, and immediately before the purification operations the molecular sieve was heated to $350\text{--}400^\circ$ and evacuated for 15–30 min. The temperature of the glass storage vessel was also increased during evacuation to reduce sorption of impurities on the wall. The total ion current passed through a maximum at 0.2–0.5 torr and then decreased continuously as the pressure was increased. Material sorbed on the interior surfaces of the mass spectrometer and the gas inlet lines also caused difficulties, and evacuation of the mass spectrometer for several days after exposure to atmospheric pressure was imperative if reliable measurements were to be made. In fact, really satisfactory measurements were obtained only after the mass spectrometer had been in continuous use in CH_4 service for several weeks.

The presence of water as an impurity could be deduced from the appearance of H_3O^+ (m/e 19) in the mass spectrum, and similarly C_2H_7^+ (m/e 31) probably was indicative of the presence of ethane. At a source pressure of 0.2 torr, H_3O^+ rather than H_2O^+ should be proportional to the water concentration, and it was estimated that the water concentration was of the order of 0.01%. The ethane concentration is not reliably known, but it is probably about the same as that for water. As a matter of interest, although the water is present in small concentration, at a source pressure of 2 torr the H_3O^+ ion comprised about 1.5% of the total ionization in the system, thus providing an illustration of the high probability of proton attachment to water and the relatively large number of collisions the ions make in the ionization chamber at high pressure.

Results

Table I contains the relative intensities (assumed to be the same as relative ion concentrations at the ion exit slit) observed at three values of the ionization chamber pressure in a typical experiment. Also included in Table I, as a matter of interest, are the relative concentrations of primary ions in methane taken from the literature. The ions tabulated at any given pressure comprise about 99.95% of the total ionization recorded on the chart issuing from the mass spectrometer. Among those omitted are ions with mass between 71 and approximately 125, which are of very small relative concentration, that is, on the order of

(9) F. H. Field and M. S. B. Munson, paper presented at the 11th ASTM Conference on Mass Spectrometry, San Francisco, Calif., May 1963.

(10) (a) V. L. Tal'roze and E. L. Frankevich, *Russ. J. Phys. Chem.*, **34**, 1275 (1960); (b) S. Wexler and R. Marshall, *J. Am. Chem. Soc.*, **86**, 781 (1964).

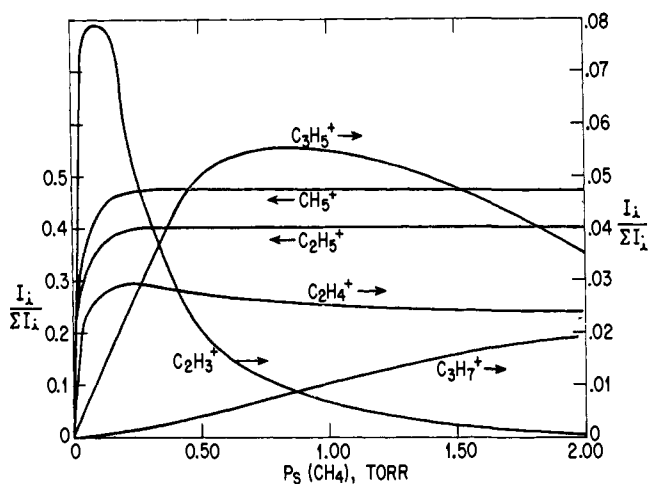


Figure 1. Relative concentrations vs. ionization chamber pressure of CH_4 .

10^{-5} or less. The variations with ionization chamber pressure of the relative concentrations of most of the important ions are shown in Figure 1. The experimental points are omitted in this figure to save space and reduce confusion, but to illustrate the experimental precision, we give in Figure 2 a pressure plot of the relative concentration for C_2H_5^+ with the experimental points included. This is reasonably typical, although for a few low concentration ions the experimental scatter was greater.

Table I. CH_4 Mass Spectra at Various Pressures (torr)^a

Ion	<i>m/e</i>	$P_s \cong 10^{-4}{}^b$	Rel. intensity, $I_i/\Sigma I_i$ at		
			$P_s = 0.34$	$P_s = 0.91$	$P_s = 1.9$
C^+	12	0.013	7.7×10^{-6}
CH^+	13	0.038	2.2×10^{-4}	4.1×10^{-5}	...
CH_2^+	14	0.076	7.7×10^{-4}	1.3×10^{-4}	...
CH_3^+	15	0.40	0.0061	8.3×10^{-4}	...
CH_4^+	16	0.47	0.0040	6.0×10^{-4}	...
CH_5^+	17	0.005	0.351	0.478	0.452
H_3O^+	19	0.0022	0.0038	0.0038	0.030
C_2H_2^+	26	4.7×10^{-4}
C_2H_3^+	27	0.039	0.0051	...	5.3×10^{-4}
C_2H_4^+	28	0.032	0.020	0.020	0.024
C_2H_5^+	29	0.440	0.406	0.406	0.349
$\text{C}_2\text{H}_7^{\text{tc}}$	31	8.5×10^{-4}	0.0012	0.0012	0.0055
C_3H_2^+	39	0.0016	5.8×10^{-4}	...	3.6×10^{-4}
C_3H_3^+	40	0.0029	0.0016	0.0016	0.0011
C_3H_4^+	41	0.086	0.055	0.055	0.053
C_3H_5^+	43	0.0047	0.0071	0.0071	0.028
C_3H_7^+	55	6.3×10^{-4}	7.0×10^{-4}	...	0.0018
C_4H_3^+	57	5.5×10^{-4}	0.0013	0.0013	0.0051
C_4H_9^+	69	7×10^{-5}	4×10^{-5}	...	0.0011
$\text{C}_5\text{H}_{11}^+$	71	6×10^{-5}	4×10^{-5}

^a Field strength (FS) = 6.25 v./cm.; electron energy (EV) = 150 v. ^b Taken from "Catalog of Mass Spectral Data," A.P.I. Research Project 44, Chemical Thermodynamics Properties Center, Texas A & M University, College Station, Texas (EV = 70 v.). ^c Intensities given are those of the higher mass (hydrocarbon) component of the doublet observed at mass 31.

CH_5^+ and C_2H_5^+ . The CH_4^+ and CH_3^+ ions are the dominant ions in the primary mass spectrum of methane, comprising about 87% of the total primary ionization. These ions react with methane according to reactions 2 and 3 to form the CH_5^+ and C_2H_5^+ ions as products, but, as may be seen from Figure 1

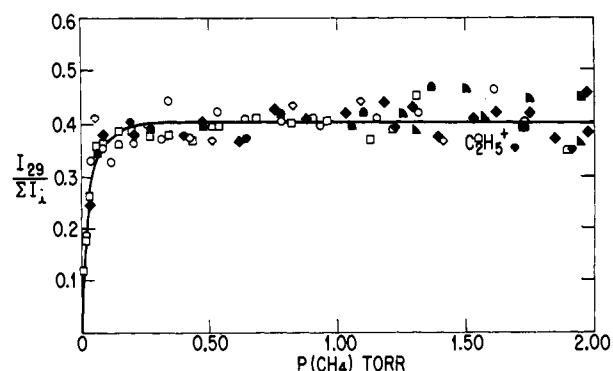
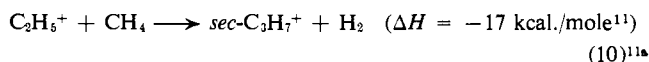


Figure 2. Relative concentrations of C_2H_5^+ vs. ionization chamber pressure of CH_4 . The different symbols represent replicate runs made over a period of about 2 months.

and Table I, these product ions are stable in methane, for no perceptible change in the ionic concentration occurs with increasing methane pressure. If one assumes that the minimum detectable change in relative intensities of these ions is about 0.05, we deduce from the observed results that the rate constants for the reactions of CH_5^+ and C_2H_5^+ with methane are smaller than approximately 10^{-12} cc./molecule sec. This nonreactivity of C_2H_5^+ is of interest since an exothermic reaction can be written for a process consuming C_2H_5^+ , namely



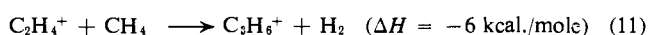
The constancy of the relative intensities of CH_5^+ and C_2H_5^+ at pressures above 0.25 torr is in disagreement with the results of previous studies on methane. Wexler and Jesse⁶ found that above a source pressure of about 0.2 torr the relative intensity of C_2H_5^+ increased steadily, but that of CH_5^+ passed through a maximum and then decreased. It was suggested that a reaction with CH_4 converting CH_5^+ to C_2H_5^+ occurs. By contrast, we have previously found⁷ that above a pressure of about 0.15 torr the CH_5^+ relative intensity continuously increased whereas the C_2H_5^+ intensity tended to decrease somewhat, and we suggested that a process forming CH_5^+ at the expense of C_2H_5^+ was occurring. In both of these contradictory studies the maximum ionization chamber pressure achieved was 0.35–0.5 torr, and the pressure range over which the conversion of C_2H_5^+ into CH_5^+ or *vice versa* could be observed was relatively limited. In the present work no net conversion of these two ions is observed over a pressure range of approximately 1.7 torr, and we believe that this finding is more reliable than those of either of the two previous works. In a subsequent paper we will consider the reactions of CH_5^+ with other compounds, which may have been impurities in the methane used by Wexler and Jesse⁶ and which can explain their results. We have no explanation for the error in our previous work,⁷ except for some instrumental effects.

(11) Heats of formation used in this paper are taken from the compilation given in F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957.

(11a) NOTE ADDED IN PROOF. As will be discussed later, this reaction may be responsible for the small amount of C_3H_7^+ actually observed, but it may still be asserted that C_2H_5^+ is effectively unreactive in methane.

Interesting comparisons can be made between the present work and the radiation chemistry studies of methane carried out by Ausloos and co-workers.^{12,13} From isotopic analyses of the products formed in the irradiations of mixtures of CH₄ and/or CD₄ in the presence of various additives, particularly perprotonated or perdeuterated higher hydrocarbons, these workers make deductions concerning the ionic reactions occurring in the system and also the radiation yields of certain ionic intermediates. Using this technique, it is found that even with as little as 0.01% of added C₃H₈ or C₄H₁₀, the majority of the ethyl ions formed in methane by reaction 3 are consumed by undergoing a hydride ion transfer reaction with the additive to produce ethane. If as an approximation we consider the cross section for the collisions of an ethyl ion with methane and propane to be equal, these results mean that on the average the ethyl ion survives approximately 10,000 collisions with methane molecules before reacting with the added propane or butane. Our results require that no reaction of the ethyl ion occurs in 50–100 collisions with methane, and thus both results indicate that ethyl ions react very slowly, if at all, with methane. Other evidence on this point is given by Ausloos and co-workers, and they also present evidence that the conversion of CH₅⁺ to C₂H₅⁺ postulated by Wexler and Jesse⁷ does not occur. We consider that with regard to the reactions of CH₅⁺ and C₂H₅⁺ the results of Ausloos and co-workers and the present results are mutually corroborative.

C₂H₄⁺. The C₂H₄⁺ ion is formed from methane by reaction 4, and, as may be seen from Table I and Figure 1, little or no further reaction of the product ion with methane occurs. The experimental scatter for this ion was for unknown reasons always relatively high, but even so there is no question that the relative intensity of C₂H₄⁺ at 2 torr is not significantly different from the value at 0.2 torr. Thus the rate constant for the reaction of this ion with methane is also on the order of 10⁻¹² cc./molecule sec. For this ion one can write an exothermic reaction with methane, namely



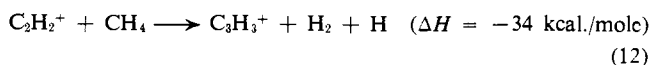
C₂H₃⁺ and C₂H₂⁺. The C₂H₃⁺ ion (*m/e* 27) is formed in methane by reaction 5, and, as can be seen from Figure 1 and Table I, it is consumed by further reaction with methane. Little doubt exists^{6,7} that C₃H₅⁺ is the product formed from C₂H₃⁺ according to the reaction 9. If this be the case, in the absence of loss processes one would expect the sum of the relative concentrations of C₂H₃⁺ and C₃H₅⁺ to be independent of the pressure of methane, but an inspection of Figure 1 shows that in fact this is not the case. We must conclude that approximately half the C₂H₃⁺ ions initially formed are lost at the higher pressures, but we are unable to account for this loss. It might be thought that a subsequent reaction of C₃H₅⁺ occurs, but no higher molecular weight product ion of concentrations comparable to the intensity loss in C₂H₃⁺ and C₃H₅⁺ is found.

From Figure 1 it may be seen that at higher pressures (above the concentration maximum) the concentration

(12) P. Ausloos, S. G. Lias, and R. Gorden, Jr., *J. Chem. Phys.*, **39**, 3341 (1963).

(13) P. Ausloos and S. G. Lias, *ibid.*, **38**, 2207 (1963).

of C₂H₃⁺ exhibits an exponential decay corresponding to pseudo-first-order kinetics. Thus we have made some logarithmic plots of the relative concentration, and a typical example is shown in Figure 3. The C₂H₂⁺ ion is formed in methane by reaction 6 and reacts further, presumably to give C₃H₅⁺,^{6,7} according to the reaction



although other products have also been reported.¹⁴ The concentrations of these ions are too small to be included conveniently in Figure 1, but we include in Figure 3 the semilogarithmic plot of the decay of the relative concentration of C₂H₂⁺. The slopes of the linear portions of the lines are equal to *kτ*, the products of the rate constants for the reactions and the residence times of the ions in the ionization chamber. Values obtained for the two ions are given in Table II (along with previously quoted rate constants), and the uncertainties are the average deviation from average of the replicate determinations.

Table II. Reaction of Product Ions in Methane

Ion	<i>kτ</i> , cc./molecule	<i>k</i> , cc./molecule sec. ^a
CH ₅ ⁺	< 2 × 10 ⁻¹⁸	< 10 ⁻¹²
C ₂ H ₅ ⁺	< 2 × 10 ⁻¹⁸	< 10 ⁻¹²
	1.2 × 10 ⁻¹⁸ ^b	0.9 × 10 ⁻¹² ^b
C ₂ H ₄ ⁺	< 5 × 10 ⁻¹⁸	< 3 × 10 ⁻¹²
C ₂ H ₂ ⁺	6.1 ± 0.9 × 10 ⁻¹⁶	4.6 ± 0.7 × 10 ⁻¹⁰
C ₂ H ₃ ⁺	1.2 ± 0.2 × 10 ⁻¹⁶	0.9 ± 0.1 × 10 ⁻¹⁰
C ₃ H ₅ ⁺	Small	Small

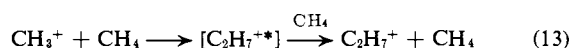
^a Calculated taking $\tau \cong \tau_{\text{C}_2\text{H}_2^+}$ (at zero pressure) = 1.3 × 10⁻⁶ sec. ^b Calculated from formation of C₃H₇⁺.

The calculation of the reaction rate constants, *k*, from these products requires a knowledge of the residence time of the ion in the ionization chamber. The choice of the proper values to use in the present experiments is not straightforward because the reactant ions are not formed at a relatively well-defined position in space (in the the electron beam) and because at the higher pressures the reactant ion undergoes a sufficiently large number of collisions with gas molecules that the time required to pass out of the ionization chamber should not be calculable from simple electrostatic considerations. Ion mobility considerations should be applied, but we do not know of the existence of information concerning the drift velocity of acetylene and vinyl ions in methane, on the one hand; and, on the other hand, we would anticipate that the drift velocities (and thus the residence time) would change as the pressure varied (the field strength was maintained constant). This should give nonlinear semilogarithmic plots of the relative concentrations, but, as one can see from Figure 3, the linearity is quite good even over the rather extended pressure range obtaining in the case of C₂H₃⁺. As a matter of interest we have calculated rate constants using residence times calculated assuming a free flight of ion from the electron beam to the ion exit slit, and these values are given in the third column of Table II.

(14) R. Barker, W. H. Hamill, and R. R. Williams, Jr., *J. Phys. Chem.* **63**, 825 (1959).

A value of $0.87 \pm 0.12 \times 10^{-10}$ cc./molecule sec. for reaction 9 has been obtained previously⁷ from studies of the pressure variation of the $C_3H_5^+$ ion. Wexler and Jesse⁶ report a cross section of 10×10^{-16} cm.² for the consumption of $C_2H_3^+$ ion at a field strength in the ionization chamber of 12.5 v./cm., and this corresponds to a rate constant of 2.7×10^{-10} cc./molecule sec. The close correspondence of the rate constants for (9) obtained in the Esso instrument is interesting. However, it will be necessary to accumulate more experience operating the mass spectrometer in the 1–2 torr pressure range before the significance of these findings can be evaluated.

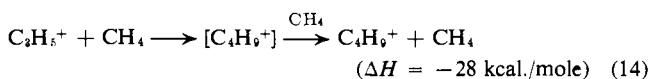
$C_2H_7^+$. Ions of m/e 31 are found in the spectra, and the peaks at this mass number are generally doublets, which we attribute to the presence of a hydrocarbon ion ($C_2H_7^+$) and an oxygenated ion (CH_3O^+). The latter is unquestionably an impurity ion and needs not be considered further. The concentration of the $C_2H_7^+$ ion varied from one batch of CH_4 introduced into the mass spectrometer to another, and the lowest relative concentration observed was about 1% at an ionization chamber pressure of 2 torr. The variation of relative concentration with pressure was approximately linear. In methane–ethane mixture studies which will be reported in a subsequent paper, it will be shown that $C_2H_7^+$ can be formed by proton transfer from CH_5^+ to C_2H_6 . Since ethane is always a possible impurity in methane, we consider that part of the $C_2H_7^+$ ion observed is the result of reaction with ethane impurity. The formation of $C_2H_7^+$ in methane alone by the three-body process



is probably quite small.

$C_3H_5^+$ and $C_3H_7^+$. As may be seen from Figure 1, the most important third-order ions are $C_3H_5^+$ (maximum relative concentration $\cong 5\%$) and $C_3H_7^+$ (maximum relative concentration $\cong 2\%$). It has been shown⁷ that $C_3H_7^+$ is formed in the reaction sequence starting with CH_3^+ , i.e., $CH_3^+ \rightarrow C_2H_5^+$ or $[C_2H_7^+] \rightarrow C_3H_7^+$, where $[C_2H_7^+]$ represents a transient complex. The ratio of the relative concentration of $C_3H_7^+$ to that of $C_2H_5^+$ is linear with pressure, and we may consider $C_3H_7^+$ is formed according to reaction 10. The value of $k\tau$ and k are tabulated in Table II. The small diminution in the concentration of $C_2H_5^+$ required by the formation of $C_3H_7^+$ by this reaction would hardly be experimentally detectable. Ausloos and Lias¹³ find $G(C_3H_7^+)/G(C_2H_5^+) = 0.064$ at methane pressures of 160 and 293 torr. In our mass spectrometer at 2.0 torr, $I_{C_3H_7^+}/I_{C_2H_5^+} = 0.048$, which comprises quite satisfactory agreement.

The concentration of $C_3H_5^+$ declines somewhat above a pressure of approximately 1 torr, but, as was discussed previously, we are unable to account satisfactorily for the loss of concentration. We consider the $C_3H_5^+$ ion to be essentially unreactive in methane, and it is of interest that an exothermic third-order reaction for its consumption can be written, namely



but this reaction occurs to a very minor extent, if at

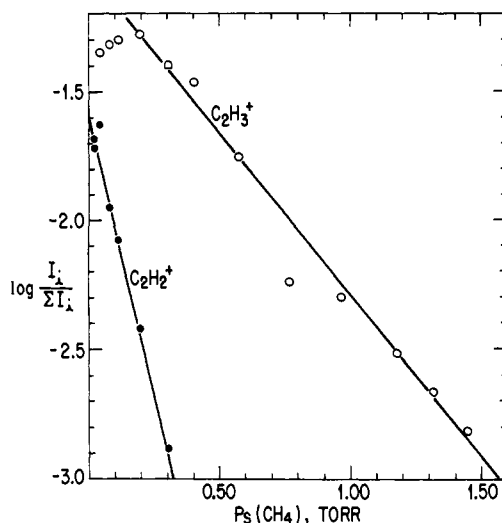


Figure 3. $\log I_i/\Sigma I_i$ vs. $P_s(CH_4)$ for $C_2H_3^+$ and $C_2H_2^+$.

all. We emphasize that the conditions are such that third-order stabilization of the sort required in (14) is quite possible under the conditions obtaining in the mass spectrometer and has, in fact, been observed to occur extensively in another system to be reported in a subsequent paper.

Thus we have encountered in this study on methane three possible reactions which are all exothermic and quite plausible, but which in fact occur only to a very limited extent. In addition, inspection of Table II shows that the rate of reaction of $C_2H_2^+$ with CH_4 is five times that of $C_2H_3^+$ with CH_4 . These observations comprise further examples¹⁵ of the operation of specific chemical factors in gaseous ionic reactions. No theoretical or conceptual framework for understanding these phenomena presently exists.

$C_4H_9^+$. As was mentioned earlier, a few ions of mass higher than m/e 43 have been observed, but the concentrations are very small, and with the exception of the ion of m/e 57, the pressure dependences of the concentrations are very weak and ill defined. The relative concentration of the m/e 57 ion ($C_4H_9^+$) increases continuously as the ionization chamber pressure increases to 2 torr, and the form of the relative concentration–source pressure plot is such as to indicate that the ion is being formed by a relatively high-order gaseous ionic process. This conclusion comprises a modification of the conclusions concerning this ion reached in our earlier study on methane.⁷

Our findings are of interest in connection with the problem of the mechanism for the formation of polymer by the high energy irradiation of methane.^{16,17} Sieck and Johnsen¹⁶ provide evidence that in the radiation of gaseous methane the polymer is formed by an ionic process. They suggest that the precursors for the polymer are hydrogen-deficient fragment ions formed from methane, i.e., C^+ , CH^+ , and CH_2^+ . Davis and Libby^{17a} provide evidence that ionic processes

(15) (a) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **68**, 3098 (1964); (b) J. L. Franklin and M. S. B. Munson, Xth International Combustion Symposium, Cambridge, England, Aug. 1964.

(16) L. W. Sieck and R. H. Johnsen, *J. Phys. Chem.*, **67**, 2281 (1963).

(17) (a) D. R. Davis and W. F. Libby, *Science*, **144**, 991 (1964); for a general consideration of hydrocarbon polymerization by ionic processes, see (b) W. F. Libby, *J. Chem. Phys.*, **35**, 1714 (1961).

are involved in the formation of polymer by the irradiation of solid methane, and they suggest that the ionic precursor to the polymer is CH_3^+ . Similar suggestions for gas phase radiolysis of methane were made by Hummel.¹⁸ The polymer formed by the solid irradiation is very similar in its properties to that formed in the gas phase irradiation. However, more recently it has been suggested that no polymer is produced in the irradiation of solid methane to very low conversions.¹⁹

The results of our mass spectrometric study provide support for the postulate of Sieck and Johnsen. The applicability of gas phase mass spectrometric studies to ionic processes in irradiated solids is not clearly established, although Libby^{17b} implies that reactions in the two phases may be appreciably different. In any event, it is clear from our results (and those of Ausloos and co-worker¹³) that in the gas phase in pure methane (1) ionic reactions involving the major ions CH_4^+ and CH_3^+ do not proceed appreciably beyond the formation of CH_5^+ and C_2H_5^+ , respectively; and (2) the small intensity of higher molecular weight product ions indicates that any ionic polymerization which is occurring involves initial reactant ions of small relative intensity. Several possibilities compatible with the present work come immediately to mind. While we think that the C_3H_5^+ ion formed in the sequence $\text{CH}_2^+ \rightarrow \text{C}_2\text{H}_3^+ \rightarrow \text{C}_3\text{H}_5^+$ is relatively

(18) R. W. Hummel, *Nature*, **192**, 1178 (1961).

(19) P. Ausloos, R. E. Rebert, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

stable in methane, we have pointed out that some loss seems to be occurring, and this conceivably could involve further reaction culminating in the formation of polymer. The CH^+ and C^+ ions formed from methane are known^{6,7} to react rapidly with methane, and the C_2H_2^+ ion formed as the first product from CH^+ reacts with methane at a very rapid rate. In fact, the subsequent reaction is so fast that the intensity of C_2H_2^+ becomes negligibly small at moderately high pressures. If the reactions of subsequent products also occur rapidly, one would expect that the product ions would not appear to a noticeable extent in the methane high pressure mass spectrum, which is in accordance with the experimental observation. Sieck and Johnsen¹⁶ find that $G(\text{polymer}) = 2.0$, and they calculate that $G(\text{CH}^+) + G(\text{C}^+) = 0.14 + 0.04 = 0.18$. If one assumes that polymer is formed by the reaction of CH^+ and C^+ , one calculates from the G values that about 11 methanes are involved in the formation of each polymer molecule. It is of considerable interest that Sieck and Johnsen report that between 12 and 20 carbons are incorporated in the polymeric chain, and Davis and Libby^{17a} report that 18 carbon atoms were involved in each polymer molecule.

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Reactions of Gaseous Ions. XV. Methane + 1% Ethane and Methane + 1% Propane

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Mass spectrometric studies have been made of gaseous ionic reactions in mixtures of $\text{CH}_4 + 1\% \text{C}_2\text{H}_6$ and $\text{CH}_4 + 1\% \text{C}_3\text{H}_8$ at pressures up to 2 torr. The ionic distribution at high pressures is very different from that in pure CH_4 . Both dissociative and nondissociative proton-transfer reactions are observed between CH_5^+ and C_2H_6 to give C_2H_5^+ and C_2H_7^+ in a ratio of 3 or 4 to 1. The proton affinity of ethane is therefore greater than the proton affinity of methane. From the formation of CH_5^+ in pure CH_4 and the dissociative proton-transfer reaction in $\text{CH}_4 + 1\% \text{C}_2\text{H}_6$, upper and lower limits for the proton affinity of methane can be determined: $115 \leq P(\text{CH}_4) \leq 121$ kcal./mole. Formation of C_3H_9^+ from proton transfer of CH_5^+ to C_3H_8 occurs to a very small extent, if at all; dissociative proton transfer to give both C_3H_7^+ and C_2H_5^+ was observed, however. Several plausible exothermic reactions which one might expect do not occur, and the nonreactivity of certain ions was established. These nonreactive ions illustrate the necessity for chemical considerations in discussing ionic reactions.

Introduction

In a recent paper¹ we have reported the ionic reactions occurring in pure methane (>99.9%) in a mass spectrometer at pressures as high as 2 torr. We observed that several of the product ions from reaction did not react further with methane and that extensive ionic polymerization involving methane did not occur. During the course of these experiments we observed that small amounts of impurities in the methane could produce major differences in the distribution of ions at high pressures. One may calculate that at 2 torr an ion will make roughly 50 collisions in passing out of the source of our mass spectrometer. If the collisions with these impurities have the usual efficiency for reaction which is characteristic of most gaseous ion-molecule reactions, one should then expect a major alteration in the distribution of ions at high pressures caused by reactions with these impurities even at concentrations of 1% or less. These findings

(1) F. H. Field and M. S. B. Munson, **87**, 3289 (1965).