

active in the hydrogen exchange. Several different physical pictures could be used to rationalize the effects of added-back water with this identification. One of these is tentatively advanced to provide an example and as a basis for further work.

It may be supposed that $i\text{-C}_4\text{H}_{10}\text{-C}^{14}$, like cumene,⁹ forms a carbonium ion by transfer of its tertiary hydrogen to the catalyst surface. This is the active species, $V(2)$. To escape, it must recapture this hydride ion or accept one by transfer from a gaseous molecule. In the latter case, a bimolecular complex may form many times before the tagged adsorbed molecule escapes, because it is trapped between the surface and the incoming molecule. If the bimolecular complex can exchange hydrogen with the catalyst, perhaps intramolecularly *via* the chemisorbed C^{14} carbonium ion, it follows that $R(D) \gg R(2)$ when the mobility of hydrogen across the surface is high and $R(D) \approx R(2)$ when it is low. Burwell¹⁶ has pointed out this difficulty of effecting the release of an adsorbed carbonium ion by hydride transfer. Accordingly, $V(1)$ is presumed to be a small portion of the easily reversibly adsorbed (possibly strongly physisorbed) hydrocarbon (0.2 cc./g. at 40 mm.) and would therefore not be expected to vary appreciably with base exchange. This is consistent with the finding that its magnitude can be greatly altered by changing the evacuation temperature.

The observation that the probability of desorption of an isolated chemisorbed isobutane molecule, $k(2)$, is independent of pretreatment or of added-back water is

(16) R. L. Burwell, Jr., H. A. Porte, and W. M. Hamilton, *J. Am. Chem. Soc.*, **81**, 1828 (1959).

of some interest. The probability is virtually zero in the absence of gaseous isobutane but becomes readily measurable under our experimental conditions. This feature was made evident in several ways. In the first place, $V(2)$ was not lowered by evacuation at 150°, instead of at room temperature, for periods of time comparable with the half-time for exchange. Secondly, no radioactivity appeared in the gas phase when the catalyst was raised to exchange temperature (if the $V(1)$ type material had been previously removed) until the $i\text{-C}_4\text{H}_{10}$ was admitted to the catalyst. This behavior could result from a mechanism involving hydride transfer from incoming gaseous molecules. Alternatively, the adsorption of a new molecule might indirectly effect the release of a chemisorbed molecule. It is hoped that work now in progress will clarify this point as well as the discrepancy between the mass transport rate, $R(2)$, and the rate of hydrogen exchange on hydrated catalysts. The effects of added-back water on the rates of isomerization, cracking, and polymerization¹⁻⁴ also remain to be elucidated.

In summary, the maximum, which has been observed in the exchange rate as a function of added-back water,^{1,5-7} can be attributed to an increased availability (or mobility) of deuterium and a decreased concentration of active chemisorbed isobutane. The simplest picture is not sufficient, however, to explain all of the facts.

Acknowledgment.—This work was sponsored by the Gulf Research and Development Co. as part of the research program of the Multiple Fellowship on Petroleum.

[CONTRIBUTION FROM THE HUMBLE OIL & REFINING CO., RESEARCH AND DEVELOPMENT, BAYTOWN, TEXAS]

Reactions of Gaseous Ions. XII. High Pressure Mass Spectrometric Study of Methane¹

BY F. H. FIELD, J. L. FRANKLIN, AND M. S. B. MUNSON

RECEIVED JUNE 7, 1963

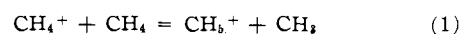
A mass spectrometric study of ionic reactions in methane was undertaken at pressures as high as 320 μ . The major secondary ions observed were CH_5^+ , C_2H_3^+ , C_2H_4^+ , and C_2H_5^+ . The major C_3 species was C_3H_5^+ formed from CH_2^+ (or C_2H_3^+); some C_3H_7^+ with the same appearance potential as CH_3^+ was observed. There was no evidence for the further reaction of CH_5^+ , but at high pressures there was evidence for the formation of CH_5^+ from CH_3^+ by a third-order reaction. C_2H_5^+ and C_2H_4^+ gave little indication of further reactions, but C_2H_2^+ reacted rapidly. No C_4 or heavier ions attributable to gas phase ionic reactions were found. The rate constants for the disappearance of CH_4^+ and CH_3^+ were found to be $9.9 \pm 0.6 \times 10^{-10}$ and $7.9 \pm 0.5 \times 10^{-10}$ cc./molecule-sec., respectively, in good agreement with previous data. The rate constants are independent of the energy of the ionizing electrons and are the same for the disappearance of CH_3^+ and CH_4^+ and the formation of C_2H_3^+ and CH_5^+ at low pressures. (Rate constants for the disappearance of all of the primary ions are approximately the same, but it appears that there are real differences among the set.) Decomposition reactions of CH_4^+ , CH_3^+ , and C_2H_5^+ caused by collision of the ions after acceleration by about 2000 v. with CH_4 molecules in the analyzer chamber were noted. The relative cross sections for decompositions decreased markedly with the number of hydrogen atoms removed. The relative cross sections for decomposition of CH_4^+ and CH_3^+ are about the same, but the cross section for decomposition of C_2H_5^+ is about four times that of CH_3^+ . Cross sections increased as the ion voltage was increased from 1000 to 3000 v., and the absolute value of the cross section for the collision-induced dissociation of CH_5^+ ions with CH_4 molecules is about 2×10^{-16} cm.² at 2000 v.

Introduction

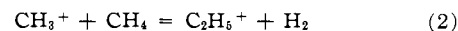
Since the reactions of hydrocarbon ions in low pressure gases have been studied in this Laboratory for some time,^{2a} it was thought worthwhile to undertake a study of the ionic reactions in gaseous hydrocarbons over the wide pressure range now accessible with the mass spectrometer at Humble with which the previous study on ethylene was made.^{2b} A study of reactions

of ions in methane at pressures as high as 300 μ is reported in this paper.

For methane the reactions



and



have been well established.³⁻⁵ Other secondary ions

(1) Supported in part by Project Squid under Contract No. Nonr-3623(S-18).

(2) (a) See, for example, F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, **84**, 1118 (1962), and earlier papers; (b) F. H. Field, *ibid.*, **83**, 1523 (1961).

(3) V. L. Tal'roze and A. L. Lyubimova, *Doklady Akad. Nauk S.S.S.R.*, **86**, 909 (1952).

(4) (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).

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

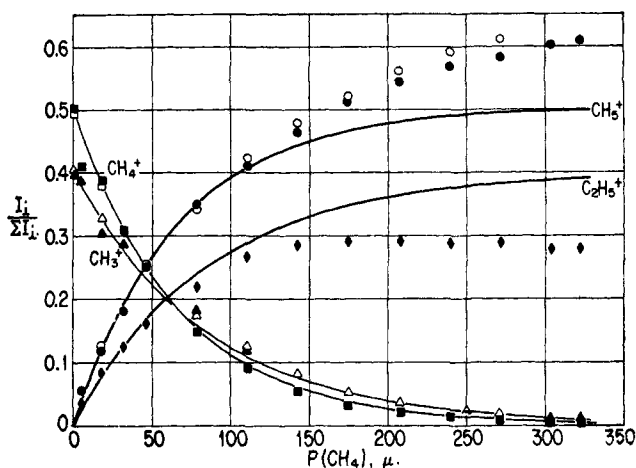


Fig. 1.—Relative concentrations of ions in CH_4 as a function of CH_4 pressure.

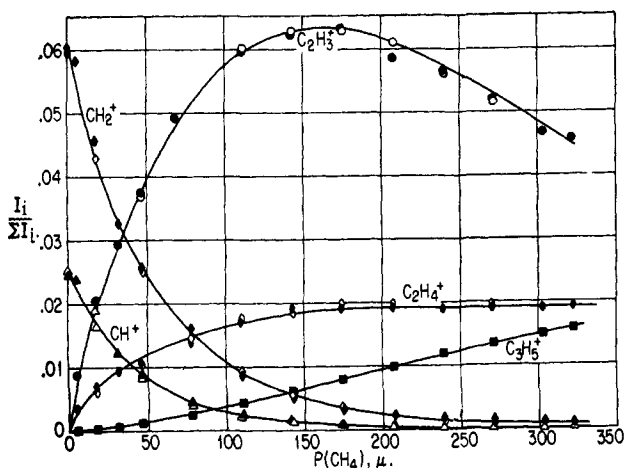


Fig. 2.—Relative concentrations of ions in CH_4 as a function of CH_4 pressure.

have also been observed,^{5,6} but at the low pressures of these studies no tertiary ions were noted. A mass spectrometric study was recently reported for CH_4 at pressures within the ionization chamber as high as 400 μ for which tertiary and higher order ions were found.⁷ Because of uncertainties in the art of high pressure mass spectrometry we feel that a corroboration of some of the data of Wexler and Jesse would be of value. Further, our data disagree with their data in several instances, and we have in addition undertaken investigations not included in their study.

Experimental

The mass spectrometer was that described by Field^{2b} but fitted with an electron multiplier as an ion detector. Mass spectra were obtained at different source pressures for different electron energies and repeller field strengths. Appearance potentials of several ions were determined by a modification of the retarding potential difference technique.⁸ The validity of and the problems involved in the measurement of appearance potentials at high pressures have been considered previously.⁹ By minor modifications it was possible to use the short source (7.0 mm.) for pressure studies and appearance potential measurements.

The methane was Phillips research grade, stated purity 99.9%, which was further purified by double fractionation. In some cases the CH_4 was distilled from Linde Molecular Sieve. It was not possible to remove water completely from the system, but its concentration was estimated to be less than 0.01%. There was some mass 18 in excess of $^{13}\text{CH}_5^+$ and mass 19, pre-

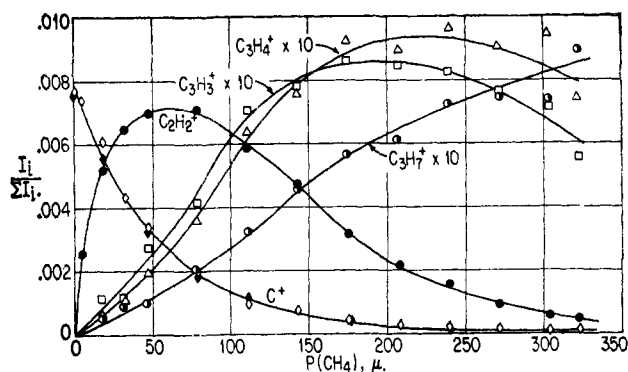


Fig. 3.—Relative concentrations of ions in CH_4 as a function of CH_4 pressure.

sumably H_2O^+ . In preliminary experiments with a larger concentration of water impurity in the methane we noted appreciable amounts of mass 31 in addition to mass 19, but this was reduced by the more extensive purification procedures.

In a series of experiments done with higher resolution obtained by fitting the mass spectrometer with narrow (0.001 in.) ion beam slits, we were able to obtain a doublet between CH_3O^+ , mass 31, from CH_3OH and mass 31 from CH_4 in a CH_4 - CH_3OH mixture at source pressures as high as 300 μ . The addition of small amounts of oxygen or water to CH_4 produced CH_3O^+ , but in a pressure study on the carefully purified CH_4 , no CH_3O^+ was observed. In the experiments with high resolution in which H_2O was added to CH_4 , the ratio $\text{CH}_3\text{O}^+/\text{H}_3\text{O}^+$ was about 3×10^{-3} , but the ratio I_{31}/I_{19} in the pressure studies reported in this paper, in which the mass 31 was not resolved into components, was about 3×10^{-2} at approximately equivalent methane pressures. Thus in these latter studies no significant amount of CH_3O^+ contributed to the mass 31 intensity. At the high source pressures required to produce C_2H_7^+ we were unable to resolve the $^{13}\text{C}_2\text{H}_5^+ - ^{12}\text{C}_2\text{H}_7^+ - ^{13}\text{C}^{12}\text{CH}_6^+$ triplet at mass 31, but contributions from $^{13}\text{C}_2\text{H}_5^+$ and $^{12}\text{C}^{13}\text{CH}_6^+$ can be calculated. After correcting for these species a net hydrocarbon intensity remained at mass 31, and consequently we feel that a small but real amount of C_2H_7^+ was observed.

As a precaution against possible contamination, the stopcock and McLeod gage, which have been used previously to measure the pressure, were removed from the system after the source pressure was determined as a function of the reservoir pressure in the manner previously reported.⁹ The residual source pressure after extended bakeout procedures was about 7×10^{-7} mm. when the source was at 240°. The highest source pressure attained was 320 μ . No background ions were observed with the operating conditions usually employed for making pressure studies, but under conditions of highest intensity (high electron current) there were observable amounts of masses 28, 29, and 32 in the background, as well as several higher mass ions (mass 55 and higher).

For the pressure studies with 70-e.v. electrons an electron current of 0.02 μa . was used. Several studies were made with electrons of lower energy (15–30 e.v.), and higher currents were used to give sufficient ion intensity for careful measurements. The source temperature varied between 180 and 240°.

Collision-induced decompositions, occurring in the analyzer tube after acceleration, were observed for several ions. The pressure in the analyzer was of the order of 10^{-4} that of the source pressure. The broad metastable peaks which were produced complicated the mass spectrum, particularly at high pressures. Some of the pressure studies from which kinetic data were obtained were made with a potential on the metastable suppressor electrode sufficient to prevent the collection of any of the ions resulting from these decompositions. The same values for the rate constants for reactions of the primary ions were obtained with and without the metastable suppressor. However, studies were also made without the metastable suppressor applied in order to obtain information about the processes producing the collision-induced ions.

Results

Figures 1, 2, and 3 show the relative intensities (ratios of ion intensity to total ionization, $I_i/\Sigma I_i$) of the prominent ions as a function of CH_4 pressure for a field strength (F.S.) of 12.5 v./cm. (maximum ion energy, E of 2.50 e.v.) and 70-e.v. electrons. Two different experiments, indicated by full and open symbols, are indicated in some cases to illustrate the reproducibility of the data, which is obviously quite good. The

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

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

(8) R. E. Fox, W. M. Hickam, D. J. Grove, and T. Kjeldaa, Jr., *Rev. Sci. Instr.*, **26**, 1101 (1955).

(9) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **67**, 1542 (1963).

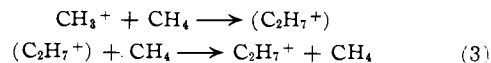
TABLE I
 RELATIVE INTENSITIES OF IONS IN METHANE

m/e	Ion	Wexler ^b and Jesse		m/e	Ion	Wexler ^b and Jesse	
		This ^a work	Jesse			This ^a work	Jesse
12	C ⁺	0.3	0.06	57		0.02	0.6
13	CH ⁺	0.6	.10	58			.1
14	CH ₂ ⁺	2	.88	60			.03
15	CH ₃ ⁺	34	7.8	61			.2
16	CH ₄ ⁺	19	2.0	63			.02
17	CH ₅ ⁺	544	326	65			.04
18	H ₂ O ⁺	1		67			.02
19	H ₃ O ⁺	2		69	0.02		.1
25	C ₂ H ⁺		0.2	71	0.01		.1
26	C ₂ H ₂ ⁺	2	0.8	73			.2
27	C ₂ H ₃ ⁺	59	112	75			.03
28	C ₂ H ₄ ⁺	19	50	76			.004
29	C ₂ H ₅ ⁺	292	390	77			.006
30	C ₂ H ₆ ⁺	0.2	12	79			.02
31	C ₂ H ₇ ⁺	.04	3	81	0.01		.03
39	C ₃ H ₃ ⁺	.8	3	83	0.01		.06
40	C ₃ H ₄ ⁺	.9	4	85			.1
41	C ₃ H ₅ ⁺	10	75	87			.06
42	C ₃ H ₆ ⁺		0.4	89			.01
43	C ₃ H ₇ ⁺	0.6	6	91			.01
44			3	93			.03
45			.6	95	0.007		.2
47			.2	97			.01
51			.3	111			.02
53			.2	121			.007
55		0.02	.4	125			.007
56		0.01	.1				

^a Pressure = 208 μ . ^b Pressure = 200 μ .

curves in Fig. 1 are calculated from our analysis of the data in a manner to be described later, but the curves in Fig. 2 and 3 are empirically drawn through the data points for the experiment. In Table I we give the relative intensities (corrected for 1.1% ¹³C) of the ions observed in methane at a source pressure of 208 μ . The intensities are expressed as parts per thousand of the total ionization, and the minimum intensity detectable under the conditions used in the experiment corresponds to a relative intensity of 0.007/1000. We have converted to parts/1000 the relative intensities given in Table I of Wexler and Jesse's⁷ paper, and for comparison we include these values in our Table I. Their measurements were made at a methane source pressure of 200 μ , but their ion path distance is 3.2 mm. rather than the 2.0-mm. value of our apparatus. Thus while one might expect a somewhat greater amount of reaction in Wexler and Jesse's apparatus because of the greater ion path length, the results given in Table I should still be comparable.

It can be seen from Table I that in our experiment at 208 μ the product ions account for about 94% of the total ionization, and the CH₅⁺ and C₂H₅⁺ ions alone account for about 84% of the total ionization. Other secondary ions formed in moderate intensity are C₂H₃⁺ and C₂H₄⁺, and the largest tertiary ion observed is C₃H₅⁺ with a relative intensity of 1%. Indeed, one may consider that this is the only C₃ ion formed, for the others observed are present at concentrations an order of magnitude smaller than that of C₃H₅⁺. An ion of mass 31 was found (relative intensity at 208 μ of 0.04/1000), and this ion is of interest because it could have the formula C₂H₇⁺, the first higher homolog of CH₅⁺. The relative abundance of the ion is very small, but its dependence on methane pressure is roughly third order. We believe that we are observing C₂H₇⁺ formed by collision stabilization in a third-order process. Wexler and Jesse also observed an ion of mass 31, presumably formed by a third-order process. Thus we suggest



From Table I it may be seen that we observe a number of high mass ions, *i.e.*, ions with masses from 55 to 125. Wexler and Jesse report the same high mass ions that we find and many more in addition. These ions must contain four or more carbon atoms, and if they are formed by ion-molecule reactions in methane, it means that methane is undergoing a very interesting type of polymerization. Wexler and Jesse postulate that indeed ion-molecule reactions are occurring, and they advance arguments to support this position. By contrast, we very strongly doubt that the high mass ions observed in our work are the result of methane ion-molecule reactions, and we believe that some aspects of the results reported by Wexler and Jesse lead one to the same conclusion about their results.

The most important reason for doubting the occurrence of ion-molecule reactions is the fact that the formation of the ions does not depend strongly enough upon the pressure of methane. To illustrate this point we give in Table II the relative intensities for the mass 43, 57, and 69 (C₃H₇⁺, C₄H₉⁺(?), and C₅H₉⁺(?)) ions at several different pressures of methane in the ionization chamber. We recognize the mass 43 ion to be an ion formed by an ion-molecule process which is third order in methane pressure, and we take the variation of $I_{43}/\Sigma I_i$ exhibited in Table II as typical of the variation to be expected for a relatively high (third) order ion-molecule reaction. By stoichiometry the orders to be expected for the formation of the mass 57 and mass 69 ions would have to be 4th and 5th, respectively, and thus one would expect the relative intensities to depend even more sharply on methane pressure. From Table II one can see that, on the contrary, the variation of relative intensity for these two ions is practically nil, which constitutes evidence against their formation by ion-molecule reactions. We observe similar behavior for all of the other ions with mass greater than 55. A number of the pressure curves given by Wexler and Jesse for these high mass ions do not seem to us to be compatible with the high order pressure dependence necessary if the ions are formed by ion-molecule reactions.

 TABLE II
 PRESSURE VARIATIONS OF RELATIVE ION INTENSITIES

Press., μ	$I_i/\Sigma I_i$ (parts/1000)		
	m/e = 43 C ₃ H ₇ ⁺	m/e = 57 C ₄ H ₉ ⁺ (?)	m/e = 69 C ₅ H ₉ ⁺ (?)
18	0.06	0.06	0
47	.10	.03	0.06
79	.20	.03	.04
111	.32	.03	.03
143	.45	.03	.03
175	.56	.03	.03
208	.61	.02	.02
240	.72	.03	.02
272	.74	.02	.01
304	.73	.02	.01
323	.89	.02	.01

On further investigation of this phenomenon we found that the ions of the same mass as most of the higher mass species produced with methane present are to be observed in the background spectrum at very high electron currents, and the relative intensities are about the same as those found in the presence of methane. No background ions are observed at normal electron currents, but one is led to think that the high mass ions can be formed from substances desorbed from the walls of the mass spectrometer by the addition of methane.

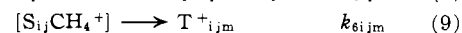
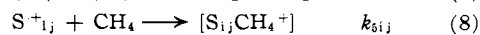
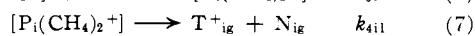
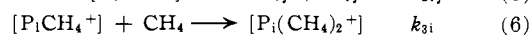
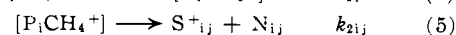
This postulate receives support from the observation that the introduction of H₂ into the mass spectrometer at about the same pressures as those used in the methane experiments produces the same high mass ions as those produced by methane. The instrument sensitivity and other instrumental conditions were the same in the experiments with H₂ and CH₄. The hydrogen used in this experiment was purified by passing it through a trap filled with charcoal and immersed in liquid nitrogen. Similar results were obtained when D₂ was introduced into the mass spectrometer, but the additions of Ar, CO₂, and SO₂ at pressures of 100–300 μ did not bring about the appearance of the high mass ions. We may rationalize these results by guessing that the high mass ions are formed from substances that are driven off the surface by gases which can undergo dissociative chemisorption on the surface (H₂, D₂, CH₄). Gases which either cannot undergo such a dissociative chemisorption or do so only with greater difficulty (Ar, CO₂, and SO₂) do not have the same effect. A rather serious flaw in this explanation results from the fact that when D₂ was passed through the mass spectrometer for about an hour with the ionization chamber at about 200°, no change in the high mass spectrum was observed to occur. If dissociative chemisorption were involved in the production of the high mass ions, one would expect that exchange with the deuterium would have occurred and that ions with somewhat different mass numbers would have appeared. Whatever may be the truth of this explanation for the phenomenon, we feel that the experiment with H₂ shows that the production of the observed high mass ions is not dependent upon the presence of methane, and taking this together with the atypical pressure dependencies for these ions when methane is present and the ever present possibility of impurities in the parts/10,000 range, we conclude that the ions of mass greater than 43 formed in the high pressure methane mass spectrum are not formed by ion-molecule reactions of methane.

When we compare our results with those of Wexler and Jesse,⁷ we find agreement with respect to the gross behavior of the system, but we find many areas of disagreement in both large and small matters. Thus they find that the intensity of the C₂H₅⁺ ion becomes about 60% greater than that of CH₅⁺, but we find that CH₅⁺ becomes about twice as great as C₂H₅⁺. Their pressure plot for the relative intensity of CH₅⁺ ion passes through a maximum and then becomes constant, whereas ours is a monotonically increasing function of pressure. In both works product ions constitute a very large fraction of the total ionization (0.944 for this work, 0.989 for Wexler and Jesse), but different distributions of the product ions were obtained. In our work the sum of the relative intensities of CH₅⁺ and C₂H₅⁺ is 0.84, whereas for Wexler and Jesse these ions comprise only 0.72 of the total ionization. The difference between these figures must be compensated by differences in other ions, and thus we see from Table I that the Wexler and Jesse values are larger than ours for ions of mass 27 (factor of 2), 28 (factor of 2.5), 30 (factor of 60), 31 (factor of 75), 41 (factor of 7.5), etc. As was mentioned previously, Wexler and Jesse find a much larger number of high mass ions than have we. Certain other differences will be discussed later in the paper. As we also mentioned previously, the ion path lengths in the two mass spectrometers used in these works are somewhat different, which might result in somewhat different results. Thus we would attribute the greater over-all amount of reaction found by Wexler and Jesse at 200 μ to this cause.

Perhaps some of the discrepancies can be resolved if we consider that they find appreciably more mass 30,

C₂H₆⁺, than we do. In a subsequent paper on reactions of CH₄ with D₂ performed under similar conditions, Wexler¹⁰ reports that C₂H₆⁺/C₂H₅⁺ is about 0.11–0.17 in the pressure range of 59–130 μ. According to Fig. 1 in the paper of Wexler and Jesse the ratio C₂H₆⁺/C₂H₅⁺ does not appear to vary up to P(CH₄) ≅ 200 μ at which pressure it is 0.031 according to their Table I. Perhaps therefore, there was a small amount of ethane in the CH₄. We found that small amounts of ethane greatly increased the relative intensity of the C₃ and higher ions when added to methane. It is also perhaps worthy of note that in the paper of Wexler and Jesse no mention was made of mass 19 (H₃O⁺) as an impurity, but it was observed with similar Phillips research grade CH₄ in the later paper of Wexler.¹⁰ The marked differences in mass 31 may be due to CH₃O⁺ which is formed if water or oxygen is present with CH₄. The mass 45 may perhaps be CO₂H⁺ since we have observed this ion to be quite prominent if CO₂ is allowed to react with a hydrogen-containing impurity.

Kinetic Analysis.—A reaction sequence



which involves the reaction of the intermediate complex [P_iCH₄⁺] in 6 and 7, as well as the reaction of the secondary ion in 8 and 9, to produce the tertiary ions has been analyzed by Lampe, Franklin, and Field.¹¹ The resultant equation for secondary ions is

$$(S_{+ij}^+) = \frac{k_{1i}k_{2ij}(P_i^+)_0}{[k_{3i}(CH_4) + \Sigma k_{2ij}][k_{1i} - k_{\delta ij}]} \left\{ e^{-k_{\delta ij}(CH_4)t_i} - e^{-k_{1i}(CH_4)t_i} \right\} \quad (10)$$

in which t_i is the residence time and $(P_i^+)_0$ is the initial concentration of P_i⁺; Σk_{2ij} refers to the possibility that more than one secondary ion may be produced by P_i⁺. For the two types of tertiary ions one obtains

$$(T_{ig}^+) = \frac{k_{4ig}}{\Sigma k_{4ig}} \frac{k_{3i}(CH_4)(P_i^+)_0}{[k_{3i}(CH_4) + \Sigma k_{2ij}]} \left\{ 1 - e^{-k_{1i}(CH_4)t_i} \right\} \quad (11)$$

for the tertiary ion formed from reaction of a complex, and

$$(T_{+ijm}^+) = \frac{k_{\delta ij m}}{\Sigma k_{\delta ij m}} \frac{k_{1i}k_{2ij}k_{\delta ij}(P_i^+)_0}{[k_{3i}(CH_4) + \Sigma k_{2ij}][k_{1i} - k_{\delta ij}]} \left\{ \frac{1 - e^{-k_{\delta ij}(CH_4)t_i}}{k_{\delta ij}} - \frac{1 - e^{-k_{1i}(CH_4)t_i}}{k_{1i}} \right\} \quad (12)$$

for the reaction of the secondary ion with another molecule of methane. Subsequent reactions of the tertiary ion are ignored. For primary ions, one obtains the simple exponential decay curve

$$(P_i^+) = (P_i^+)_0 e^{-k_{1i}(CH_4)t_i} \quad (13)$$

Wexler and Jesse⁷ express the kinetics in terms derived from the attenuation of a beam of ions, and their equations are equivalent to ours. However, the equivalence is not exact for consecutive reactions and reactions where more than one secondary ion is formed from a primary ion.

If one assumes that ion intensity (peak height) is proportional to ion concentration with the same proportionality constant for all ions, and that the fragmentation pattern of the initial excited CH₄⁺ is inde-

(10) S. Wexler, *J. Am. Chem. Soc.*, **85**, 272 (1963).

(11) F. W. Lampe, J. L. Franklin, and F. H. Field, in "Progress in Reaction Kinetics," Vol. I, Pergamon Press, New York, N. Y., 1961, pp. 73–79.

pendent of pressure, then one obtains for the primary ions

$$\ln(I_i/\Sigma I_i) = \ln \bar{A}_i - k_{1i}(\text{CH}_4)t_i \quad (14)$$

for which $(P_i^+)_0 = \bar{A}_i \Sigma I_i$; $t_i = (2dM_i/eF.S.)^{1/2}$, for which d is the ion path in the source, M_i is the mass of P_i , e is the electronic charge, and $F.S.$ is the field strength in the source.

Primary Ions.—The primary ions, which appear to have reasonable exponential decay curves in Fig. 1, 2, and 3, are therefore plotted on a logarithmic scale as a function of pressure in Fig. 4. The linearity of the logarithmic plots for CH_4^+ and CH_3^+ over the wide pressure range is excellent. The deviations from linearity of the other primary ions at high pressures is not considered to be disquieting. While the curves for the disappearance of C^+ , CH^+ , and CH_2^+ may possibly be considered as composite curves of two processes with different rate constants, it also seems possible that the curvature may be the result of adventitious instrumental phenomena; *i.e.*, ionization of pyrolysis products or other reaction products, or reaction of ions formed in different areas of the source which become noticeable only when the concentration of the normally formed ions is small, etc. It does not appear to us that this deviation warrants extended discussion. The rate constants for the disappearance of the primary ions are determined from the slopes of the initial linear portions of the curves.

Table III shows rate constants (and cross sections) for the disappearance of the primary ions from several experiments with 70-e.v. electrons. The agreement among the values for the rate constants was very good as indicated by the average deviation. The rate constants for the disappearance of the ions are about the same, as would be predicted if the rate constants depended solely on the polarizability of the neutral molecule. The differences among the rate constants appear to be greater than the experimental errors, however. The rate constants for the disappearance of CH_4^+ and CH_3^+ in Table III include data taken at temperatures from 180–240°; there is no variation of the rate constants within this temperature range.

TABLE III

RATE CONSTANTS AND CROSS SECTIONS FOR DISAPPEARANCE OF PRIMARY IONS OF CH_4 AT $F.S. = 12.5 \text{ V./CM.}$ AND $E.V. = 70 \text{ V.}$

Ion	k_i cc./molecule-sec. $\times 10^{10}$	Q_i $\text{cm.}^2 \times 10^{16}$
CH_4^+	$10.3 \pm 0.3 (8)^a$	38
CH_3^+	$8.2 \pm 0.3 (8)^a$	29
CH_2^+	$12.4 \pm 1.3 (4)^a$	41
CH^+	$17.4 \pm 1.6 (4)^a$	56
C^+	$13.1 \pm 1.3 (4)^a$	42

^a Number of replicate determinations.

The data of Table IV show that there is essentially no variation in the rate constants for the disappearance of the primary ions with changes in electron energy. The electron energies are only approximate since there is an electric field present to drive the ions out of the source. Although the data show more scatter than the data in Table III, the agreement is good. The observed invariance of rate constants indicates that the reactions involve only ground-state ions, since one would expect that the ratio of concentrations of excited ions to ground-state ions would vary with electron energy.

Secondary Ions.—In order to obtain rate constants for the formation of a secondary or tertiary ion one must know the corresponding primary ion and be certain that the secondary ion is formed, at least pre-

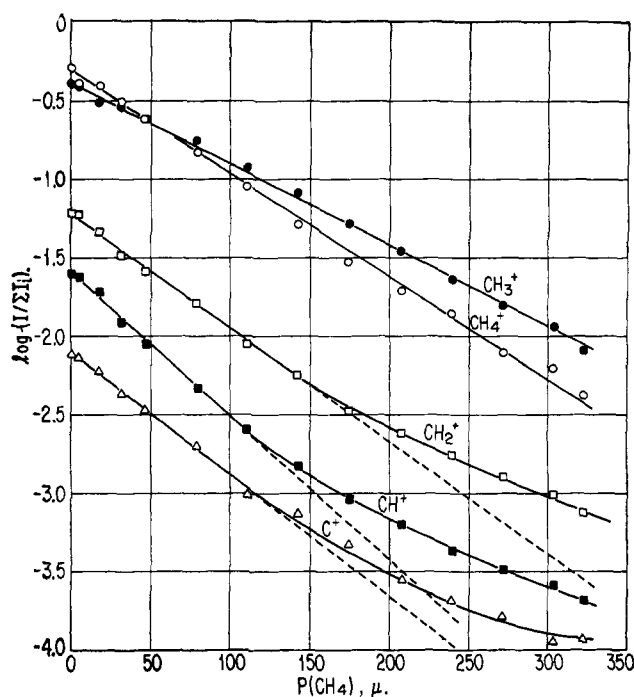


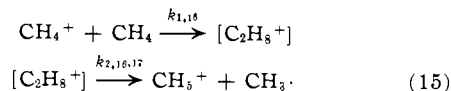
Fig. 4.—Semilogarithmic plot of relative primary ion concentrations as a function of methane pressure

dominantly, from one primary ion. Table V shows the appearance potentials for several of the ions in methane and the primary ion corresponding to this energy. The ionization efficiency curves for C_2H_4^+ showed a discontinuity at about 15.5 e.v., indicating that it is formed by two processes. For the other ions whose appearance potentials were determined, the ionization efficiency curves did not provide conclusive evidence for their formation by more than one process.

One can establish the contributions of different primary ions to each product ion by measuring the rate constants for the formation of the ions at different electron energies; that is, at different ratios of primary ions. One can also establish whether or not a primary ion reacts by more than one path by comparing the rate constant for the disappearance of the primary ion with the rate constant for the formation of the secondary ion.

Using these considerations we made a kinetic analysis of the product ions which, for convenience, are grouped according to the primary ion or complex from which the product ions are formed.

(C_2H_3^+), Ions Formed from CH_4^+ .—As a first approximation we may postulate that the complex (C_2H_3^+) formed from the reaction of CH_4^+ undergoes no further reaction and decomposes only to yield CH_3^+ ; that is, the reactions occurring are



The rate constant notation follows that given in the general eq. 4–9. For eq. 15, 10 can be rewritten in the form

$$I_{17}/\Sigma I_i = \bar{A}_{16}(1 - e^{-k_{1,16}(\text{CH}_4)t_{16}}) \quad (16)$$

where \bar{A}_{16} is the fraction of mass 16 ions in the total ionization of methane before any ion-molecule reactions occur. The value for $k_{1,16}$ calculated from the disappearance of CH_4 is the value given in Table III, $10.3 \pm 0.3 \times 10^{-10}$ cc./molecule-sec., and the values of $I_{17}/\Sigma I_i$ calculated from 16 using this value of $k_{1,16}$ are plotted as the line labeled " CH_3^+ " in Fig. 1. It is clear that the

TABLE IV
EFFECT OF ELECTRON ENERGY ON RATE CONSTANTS, $k \times 10^{10}$
F.S. = 12.5 v./cm.

E.v.	CH ₄ ⁺	CH ₃ ⁺	CH ₂ ⁺	CH ⁺	C ⁺
10.5	10.4				
15	9.4	7.3	12.7		
20	7.9	7.1	11.8		
30	8.6	6.9	10.0	13	~12
70 (av.)	10.3	8.2	12.4	17.4	13.1
Av. of all data	9.9 ± 0.6	7.9 ± 0.5	12.0 ± 1.1	16.5 ± 1.8	13.1 ± 1.3
Av. Q, cm. ²	36 × 10 ⁻¹⁶	28 × 10 ⁻¹⁶	41 × 10 ⁻¹⁶	54 × 10 ⁻¹⁶	42 × 10 ⁻¹⁶

TABLE V
APPEARANCE POTENTIALS OF IONS IN METHANE

Ion	A.P., e.v.	Primary ion
CD ₅ ⁺	13.1 ± 0.1	CD ₄ ⁺
C ₂ H ₃ ⁺	15.5 ± .1	CH ₂ ⁺
C ₂ H ₄ ⁺	13.0 ± .1	CH ₄ ⁺
	Break ~15.5	CH ₂ ⁺
C ₂ H ₅ ⁺	14.2 ± 0.2	CH ₃ ⁺
C ₃ H ₅ ⁺	15.4 ± .1	CH ₂ ⁺
C ₃ H ₇ ⁺	14.4 ± .1	CH ₃ ⁺

TABLE VI
REACTIONS OF CH₄⁺, $k_{1i} = 1.0 \times 10^{-9}$ CC./MOLECULE-SEC.

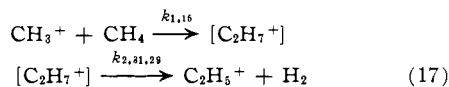
Reaction	ΔH , kcal./mole	$k_{2ij}/\Sigma k_{2ij}$
CH ₄ ⁺ + CH ₄ → CH ₅ ⁺ + CH ₃		1.0
→ C ₂ H ₅ ⁺ + H ₂ + H	+ 9	≤ 1 × 10 ⁻³
→ C ₂ H ₆ ⁺ + H ₂	-18	~2 × 10 ⁻⁴
→ C ₂ H ₄ ⁺ + 2H ₂	-12	1-3 × 10 ⁻³
→ C ₂ H ₃ ⁺ + 2H ₂ + H	+65	≤ 5 × 10 ⁻⁶
→ C ₂ H ₂ ⁺ + 3H ₂	+50	≤ 5 × 10 ⁻⁶

calculated and experimental values are in good agreement for methane pressure below about 120 μ , but above this pressure the experimental values of the relative intensity of CH₅⁺ increase above the calculated values. Indeed, the experimental values increase above the initial relative concentration of CH₄⁺ in the methane mass spectrum. Discussion on these points will be deferred until somewhat later.

From the values of $I_{17}/\Sigma I_i$ at pressures below 120 μ one can calculate a value of $k_{1,16}$ from 16 of 10.5×10^{-10} cc./molecule-sec. This value is the same as the value for $k_{1,16}$ calculated from the disappearance of CH₄⁺; therefore, we conclude that CH₄⁺ produces CH₅⁺ almost exclusively.

While it is not possible to state unequivocally that other reactions do not occur, from pressure studies at low electron voltages, such that essentially only CH₄⁺ is formed as a primary ion, we can estimate upper limits for other reactions. The upper limits for the fractional dissociation of (C₂H₃⁺) to other possible secondary products are given in Table VI. According to our appearance potentials some C₂H₄⁺ is formed from CH₄⁺ and the observed small amount of C₂H₆⁺ may be accounted for by this reaction. The low relative fractions of dissociation of the complex to give C₂H₆⁺ and C₂H₄⁺ (despite the fact that the reactions are exothermic) are compatible with the loose complex suggested by experiments on mixtures of CH₄ and CD₄,¹² implying very weak C-C bond formation.

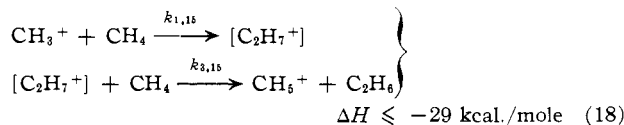
(C₂H₇⁺), Ions Formed from CH₃⁺.—The C₂H₅⁺ ion is known to be formed from the following set of reactions



(12) C. D. Wagner, P. A. Wadsworth, and D. P. Stevenson, *J. Chem. Phys.*, **28**, 517 (1958).

The value of $k_{1,15}$ calculated from the disappearance of CH₃⁺ and given in Table III is $8.2 \pm 0.3 \times 10^{-10}$ cc./molecule-sec. Values of $I_{29}/\Sigma I_i$ have been calculated using this value in the analog of 16, and the values thus obtained are plotted as the solid line labeled "C₂H₅⁺" in Fig. 1. It may be seen that the calculated values are in satisfactory agreement with the experimental values below a methane pressure of about 100 μ , but above this pressure the experimental values fall beneath the calculated values. The values of $k_{1,15}$ calculated from C₂H₅⁺ relative intensity in the low pressure region is $7.9 \pm 0.4 \times 10^{-10}$ cc./molecule-sec., and the good agreement with the value obtained from CH₃⁺ disappearance may be taken to mean that in the low pressure region CH₃⁺ gives almost exclusively C₂H₅⁺.

From Fig. 1 it may be seen that the experimental relative intensities of C₂H₅⁺ ion fall significantly below the initial concentration of the reactant CH₃⁺ ion relative intensity, which suggests the possibility that CH₃⁺ is reacting to form appreciable amounts of an ion other than C₂H₅⁺. From Fig. 1 and the preceding discussion it is obvious that excess CH₅⁺ is formed, and in about the same amount as the loss of C₂H₅⁺. We may write the exothermic third-order reaction



and since the reaction proceeds through the complex (C₂H₇⁺), it will not alter the exponential equation for the disappearance of CH₃⁺. If we assume the difference between the calculated and experimental CH₅⁺ intensities, $\Delta(\text{CH}_5^+)$, to result from the occurrence of 18, we can show from 10 and 11 that

$$\frac{\Delta(\text{CH}_5^+)}{(\text{C}_2\text{H}_5^+)} \cong \frac{k_{3,15}}{k_{2,15,29}} (\text{CH}_4) \quad (19)$$

An analogous equation can be written for the loss of C₂H₅⁺ ions. Plots of $\Delta(\text{CH}_5^+)/(\text{C}_2\text{H}_5^+)$ and $\Delta(\text{C}_2\text{H}_6^+)/(\text{C}_2\text{H}_5^+)$ are approximately linear functions of CH₄ pressure, but do not pass through the origin. Both the slope and the intercept of these curves are sensitive functions of $k_{1,15}$, $k_{1,16}$, and the values of (CH₄⁺)₀ and (CH₃⁺)₀ so that the derived value of $k_{3,15}/k_{2,15,29}$, 1.0×10^{-16} cc./molecule, is only approximate.

We tentatively postulate that some CH₅⁺ ions are formed from CH₃⁺ by the third-order process written in 18. This postulate is, however, contrary to the findings of Wexler and Jesse,⁷ who found that the CH₅⁺ relative intensity decreases at high pressures, whereas that of C₂H₅⁺ increases. Thus they postulate that CH₅⁺ undergoes subsequent reactions with methane. If our postulate is correct, from Fig. 1 it may be seen that at 300 μ , CH₅⁺ formed by the third-order process 18 constitutes about 10% of the total ionization in CH₄. C₂H₆ is written as the neutral product in 18, and thus this reaction may be involved in the production of C₂H₆ in the radiation chemistry of methane.

Two other tertiary ions may involve the $(C_2H_7^+)$ complex as an intermediate. These are the $C_2H_7^+$ ion observed at mass 31 (which surely involves the $(C_2H_7^+)$ complex) and the $C_3H_7^+$ ion observed at mass 43 with an appearance potential equal to that of the CH_3^+ ion.

For tertiary ions formed from reactions proceeding through an intermediate complex we may use 11 or an expansion valid in the pressure region for which the tertiary ions are present only in a low relative abundance

$$\frac{T_{ig}^+}{(P^+)_{ig}} = \left(\frac{k_{4ig}}{\Sigma k_{4ig}} \right) \left(\frac{k_{11}k_{31}}{\Sigma k_{21j}} \right) (CH_4)^2 \quad (20)$$

to obtain the effective third-order rate constant, $(k_{4ig}/\Sigma k_{4ig})(k_{11}k_{31}/\Sigma k_{21j})$. For $C_2H_7^+$ the data are badly scattered and not highly reproducible, but from the low pressure slope of a plot of $(C_2H_7^+)/((CH_3^+)_0)$ against the square of the methane pressure we estimate the effective third-order rate constant to be not greater than 10^{-29} cc.²/molecule²-sec. The data for $C_3H_7^+$ are more consistent, and by similar calculations we obtain a value of 2.4×10^{-28} cc.²/molecule²-sec. with 15–30-v. electrons for the effective third-order rate constant

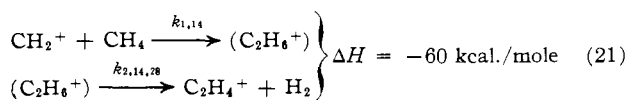
$$(k_{4,15,43}/\Sigma k_{4,15g})(k_{1,15}k_{3,15}/\Sigma k_{2,15g})$$

From experiments with 70-e.v. electrons we obtain a value of 4.0×10^{-28} cc.²/molecule²-sec. for the latter quantity. We have no explanation for the difference between the two values. The same values for the rate constants can be obtained from 11 which is valid over the whole pressure range. It is possible that $C_3H_7^+$ can be formed from $C_2H_5^+$ rather than from the $(C_2H_7^+)$ complex and the kinetic data do not allow us to make a firm choice, but we prefer to consider the latter case.

The value for the third-order rate constant for the formation of $C_3H_7^+$ is about a factor of ten smaller than the values obtained for tertiary ions in C_2H_4 .^{2b} If our postulate concerning the third-order formation of CH_5^+ from CH_3^+ , (18), is correct, then this small value of the rate constant is the result of a small relative dissociation of the complex $[C_3H_{11}^+]$ to give $C_3H_7^+$, $k_{4,15,43}/\Sigma k_{4,15,1}$, the fractional dissociation to $C_3H_7^+$, may be determined as about 0.04 from the ratio $(C_3H_7^+)/[(C_3H_7^+) + (\Delta CH_5^+)]$. We would then obtain a value of 6×10^{-27} cc.²/molecule²-sec. for the third-order rate constant, which is compatible with the values found previously for C_2H_4 .

Table VII shows a compilation of rate constants and cross sections for reactions of CH_3^+ and CH_4^+ with CH_4 from the available literature. The agreement among the workers is satisfactory for values of the rate constants, which suggests that the absolute values of these rate constants are known with a precision approaching that for ordinary rate constant measurements. The data of Table VII indicate that k is independent of ion energy or field strength in this range, although this may be in disagreement with the data of Field, Franklin, and Lampe,⁵ which indicated a decrease in k with increasing ion energy.

$(C_2H_6^+)$, Ions Formed from CH_2^+ .—From its ionization efficiency curve $C_2H_4^+$ is formed from both CH_4^+ and CH_2^+ . Making a correction for the formation of $C_2H_4^+$ from CH_4^+ and using the value of the rate constant for the formation of $(C_2H_6^+)$, $k_{1,14}$, obtained from the disappearance of CH_2^+ together with the zero pressure value of $(P^+)_{ig}$, we obtained 0.312 ± 0.057 for the fractional decomposition of the $(C_2H_6^+)$ complex into $C_2H_4^+$ as the average of all the experiments. Thus



and $k_{2,14,28}/\Sigma k_{2,14,j} = 0.312$.

TABLE VII

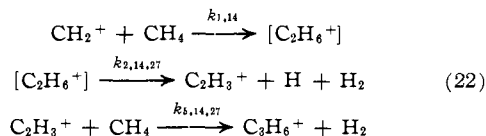
COMPARISONS OF RATE CONSTANTS FOR THE REACTIONS OF CH_4^+ AND CH_3^+ WITH CH_4 OBTAINED BY DIFFERENT WORKERS

F.S.	E_{max}	CH_4^+		CH_3^+	
		k , cc./molecule-sec. $\times 10^{10}$	Q , cm. ² $\times 10^{18}$	k , cc./molecule-sec. $\times 10^{10}$	Q , cm. ² $\times 10^{18}$
2	0.10	5.0	55	4.8	51 ^a
6	0.30	8.0	68	7.0	58
20	1.0	8.4	45	8.8	46
40	2.0	7.0	27	7.4	28
100	5.0	2.2	5.6	3.4	8.4
?	?	13.8 ^b			
		0.1			163
		1.0			39
	~0.05	11.6 ^c	175		
6.7	0.66			15.8	108 ^d
13.3	1.35			10.3	50
20.0	2.00			8.1	32
12.5	4.00	13.6	39	9.6	27 ^e
12.5	2.50	9.9 \pm 0.6	36	7.9 \pm 0.5	28 ^f

^a Ref. 5. ^b Ref. 4. ^c V. L. Tal'roze and E. L. Frankevich, *Russ. J. Phys. Chem.*, **34**, 1275 (1960). ^d Ref. 6. ^e Ref. 7. ^f These data.

$C_2H_3^+$ appears to be formed from CH_2^+ according to the appearance potential measurements, but the reaction for its formation is endothermic by about 17 kcal./mole. It is disconcerting that the major product of an ion-molecule reaction should be one formed by an endothermic process, as this is generally not the case. We remeasured the appearance potential of CH_2^+ and obtained the value of 15.5 e.v., which could give $\Delta H_f(CH_2^+)$ as 340 kcal./mole. If $\Delta H_f(C_2H_3^+)$ were about 270 kcal./mole, the reaction would be thermoneutral, but the electron impact values from many sources are all about 280 kcal./mole.¹³

In Fig. 2 it may be seen that the curve for $C_2H_3^+$ passes through a maximum, which indicates that $C_2H_3^+$ is involved in the formation of a tertiary product ion. The ion formed is doubtless $C_3H_5^+$ since, as may be seen from Table V, both $C_2H_3^+$ and $C_3H_5^+$ are formed from CH_2^+ . The ratio I_{41}/I_{27} increases more than linearly with pressure and increases markedly with a decrease in field strength from 12.5 to 3.8 v./cm. These changes are not in agreement with predictions of the behavior of a tertiary ion formed through an intermediate complex. The ratio of 11 to 10 (with $k_{6ij} \cong 0$) predicts a linear dependence of I_{41}/I_{27} against methane concentration over the entire pressure range if $C_3H_5^+$ results from reaction of the $(C_2H_6^+)$ complex. This behavior is not observed. The ratio of 12 to 10 is a much more complex function but does not, in general, predict a straight-line relationship. Further, the ratio of 11 to 10 does not include time explicitly, whereas the ratio of 12 to 10 does include time explicitly and in the approximate form shows that $C_3H_5^+/C_2H_5^+$ should increase as the field strength decreases. For these reasons we consider that $C_3H_5^+$ is formed by reaction of the secondary ion, $C_2H_3^+$, with methane according to the mechanism



The quantity $I_{41}/\Sigma I_i$ is plotted against the square of the ionization chamber pressure in Fig. 5, and the form of the curve is that which one would expect from 12 for a tertiary ion. The value for the rate constant $k_{3,14,27}$ was

(13) References to heats of formation of the ions are from F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

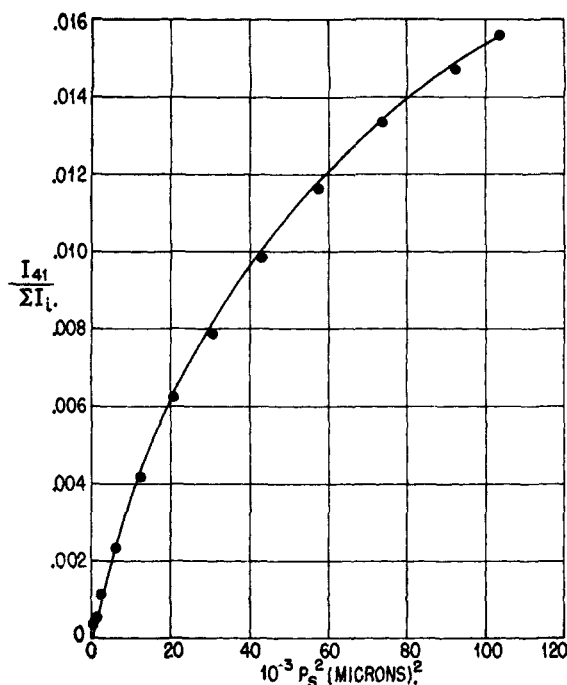


Fig. 5.—Relative intensity of $C_3H_5^+$ as a function of $(P_s(CH_4))^2$.

obtained by substituting current ratios such as those shown in Fig. 5 in 12 and solving the equation for the value of the rate constant. This computation was facilitated by using an electronic digital computer. The value of $k_{1,14}$ was taken from Table III; $k_{31}(CH_4)$ was considered to be negligible compared with $\sum k_{2ij}$, and $k_{6ijm}/\sum k_{6ijm}$ was taken to be unity. It was pointed out above that about 31% of the $(C_2H_6^+)$ complex formed from CH_2^+ and CH_4 decomposes to give $C_2H_4^+$ ion. In addition we have evidence which leads us to think that about 5% of the complex decomposes to yield $C_2H_2^+$ ions, and consequently in 12 we use the value 0.64 for $k_{2,14,27}/\sum k_{2,14,j}$. The average for all the values of $k_{5,14,27}$ calculated from 12 is $8.7 \pm 1.2 \times 10^{-11}$ cc./molecule-sec., and this average includes values from experiments done at different electron energies and field strengths. This value for a second-order rate constant is somewhat lower than those for the reaction of the primary ions in methane, but it is still in the range of those found in many ion-molecule reactions.

Taking the observed fractional dissociations of the complex $(C_2H_6^+)$ as 0.05 to $C_2H_2^+$, 0.64 to $C_2H_3^+$, and 0.31 to $C_2H_4^+$, and comparing these fractions with the fractions of total ionization of these ions from the mass spectrum of C_2H_6 —0.15, $C_2H_2^+$; 0.21, $C_2H_3^+$; and 0.64, $C_2H_4^+$ —we cannot see any resemblance of the $(C_2H_6^+)$ complex to the ethane ion.

Since we observe a greater concentration of products of CH_2^+ than the initial concentration of CH_2^+ and cannot account for most of the CH^+ which has reacted, we consider the fractional dissociations of $C_2H_6^+$ to be only approximate, since they will vary markedly with the reaction products of CH^+ .

Other Ions.— $C_2H_2^+$ comes partly from CH_2^+ as indicated above, but the ratio I_{26}/I_{27} (extrapolated to zero pressure) increases with electron energy, 0.07 at about 20 e.v. to about 0.30 at 70 e.v., so that $C_2H_2^+$ is formed from another ion as well, probably CH^+ . Because of the uncertainties in the precursors and products of $C_2H_2^+$, no quantitative kinetics were attempted. $C_3H_4^+$ also appears to come from CH^+ but the ratio I_{38}/I_{40} increases with increasing electron energy so that $C_3H_3^+$ arises at least partly from an even higher energy ion, C^+ .

Our reaction sequences for the main ions are in agreement with those of previous workers. We find that CH_4^+ gives CH_5^+ , $C_2H_6^+$ (in agreement with Wexler and Jesse⁷), and $C_2H_4^+$ (which they indicate as coming from CH_3^+ , a very endothermic process), and we do not observe meaningful quantities of the other ions they attribute to CH_4^+ . We find CH_3^+ producing $C_2H_5^+$, $C_3H_7^+$, $C_2H_7^+$, and probably CH_5^+ , but we do not observe meaningful quantities of the higher ions attributed by Wexler and Jesse to CH_3^+ . Fuchs⁶ observed $C_2H_2^+$ as a reaction product of CH_2^+ , and Wexler and Jesse report it as coming from CH^+ , while we find that it comes from both ions, but predominantly from CH^+ .

We find $C_2H_3^+$ and $C_3H_5^+$ coming from CH_2^+ as do Wexler and Jesse; but Fuchs obtained a value of 17.1 as the appearance potential of $C_2H_3^+$, which led him to attribute its formation to reaction of excited CH_2^+ or CH_3^+ . We find $C_3H_3^+$ and $C_3H_4^+$ as arising from different reactant ions, whereas Wexler and Jesse attribute both to CH^+ . We can make no comparisons of our appearance potentials with those of Wexler and Jesse since they give no values.

Dissociation Processes.—As the source pressure was increased, diffuse peaks were observed in the spectra, presumably due to reactions occurring in the analyzer tube after the ions had been accelerated to 2000 v., but before they reached the strong analyzing magnetic field. At about 250μ the diffuse peaks accounted for 3–5% of the total intensity. Assuming that the diffuse peaks are the result of collision-induced dissociations, one may calculate the actual masses involved from the equation

$$m^* = m_i^2/m_f \quad (23)$$

in which m^* is the observed mass of the ion, m_f is the final ion, and m_i is the initial ion which decomposes.

Many diffuse peaks were observed, but only for some of the peaks was an unambiguous assignment possible. By adjusting the electron and repeller voltages, the kinds of ions formed in the ionization chamber could be controlled, and under these conditions a number of reactions involving decompositions of CH_5^+ , CH_4^+ , and $C_2H_5^+$ could be identified. The assignment was based on agreement of calculated and observed mass number and the constancy of the ratio of intensity of diffuse peak to assumed parent peak as a function of electron energy. For all of the processes which we identified, the ratio of diffuse peak to parent peak—for example, $I_{14,9}/I_{17}$ —increased approximately linearly with pressure in the analyzer (or source envelope or source pressure), so that the processes observed were collision-induced decompositions.

Table VIII shows some of the processes noted; the ion energy for these experiments was 2000 v. The observed mass numbers are within about one-tenth of a mass unit of the calculated values. The relative cross sections for the decomposition of the same ion to different products (the ratio of diffuse ion intensities) decrease markedly with the number of hydrogens removed from the molecule.

Because of the breadth of the beam of the collision-induced ions, the peak intensity (peak height) is not an accurate measure of the total beam intensity. The relation between the observed diffuse peak intensity and the total intensity of a given collision-induced ion is

$$I_i = I_{av}wD/ds \quad (24)$$

I_i is the total intensity of the beam of ions; I_{av} is the observed average intensity, $\int I(w)w/w$; w is the width of the diffuse peak measured at the base line; d is the distance between two masses; D is the dispersion, $R\Delta M/M$, in which R is the radius of curvature of the ion path, 30 cm., and M is the mass of an ion; and s is

TABLE VIII
 COLLISION-INDUCED DECOMPOSITION OF IONS FROM CH₄

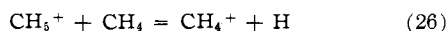
	ΔH_f kcal./mole	m^*		$Q_{rel.}$ at 2000 v.
		Calcd.	Obsd.	
(CH ₅ ⁺)				
CH ₅ ⁺ → CH ₄ ⁺ + H	+101	15.06	14.9	1.00
→ CH ₃ ⁺ + H ₂ (2H)	26 (129)	13.23	13.2	0.39 ± 0.03
→ CH ₂ ⁺ + H ₂ + H (3H)	149 (253)	11.52	11.5	.047 ± .008
→ CH ⁺ + 2H ₂ (4H)	124 (330)	9.94	10.0	.012 ± .002
→ C ⁺ + 2H ₂ + H (5H)	211 (417)	8.47	8.4	.005
(CH ₄ ⁺)				
C ₂ H ₅ ⁺ → C ₂ H ₄ ⁺ + H	+83	27.1	26.9	1.00
→ C ₂ H ₃ ⁺ + H ₂ (2H)	56 (159)	25.2	25.2	0.26 ± 0.03
→ C ₂ H ₂ ⁺ + H ₂ + H (3H)	145 (248)	23.3	23.1	.049 ± .005
→ C ₂ H ⁺ + 2H ₂ (4H)	190 (396)	21.6	21.2	.005 ± .001
(CH ₄ ⁺)				
CH ₄ ⁺ → CH ₃ ⁺ + H	29	14.06	14.1	1.00
→ CH ₂ ⁺ + H ₂ (2H)	48 (151)	12.25	12.3	0.19

the actual width of the collector slit (0.017 in.). The calculated I_t differed from the peak heights by not more than 50%.

For a small extent of reaction of a second-order process, expansion of 10 or its equivalent in terms of cross section will give

$$I_m/I_p = Qd(\text{CH}_4) \quad (25)$$

for which I_m represents the intensity of the diffuse peak and I_p represents the intensity of the parent peak. From the slope of a plot of the ratio of diffuse peak to parent peak as a function of pressure in the analyzer tube one can obtain the cross section. The distance, d , was taken to be the distance between the entrance to the analyzer and the magnet, about 51 cm. The analyzer pressures are not accurate nor is this distance, d , more than an approximate measure of the path length over which collectable collision-induced ions may be formed, but these values should give an order of magnitude estimate of the cross section. We obtain a cross section of about 2×10^{-16} cm.² for the reaction



Since the cross sections increase with increasing ion energy (see below) and the rate constants calculated in the usual fashion would increase even more rapidly with ion velocity, we have used cross sections as the more meaningful quantity in the discussion of the collision-induced processes.

Taking the ratio of the quantities I_m/I_p for dissociation of two ions we can obtain the relative cross sections for the collision-induced dissociations of these two ions. $Q(\text{CH}_5^+ \rightarrow \text{CH}_4^+)/Q(\text{C}_2\text{H}_5^+ \rightarrow \text{C}_2\text{H}_4^+)$, the ratio of the main modes of decomposition of CH₅⁺ and C₂H₅⁺, is 0.26; that is, the cross section for the decomposition of C₂H₅⁺ induced by collision with CH₄ molecules is about

four times that of CH₅⁺. The cross section for the dissociation of CH₄⁺ is about the same as the cross section for dissociation of CH₅⁺.

Collision-induced reactions of the primary ions in methane have been observed previously,¹⁴ and it is gratifying to note that our relative cross section for the decomposition of CH₄⁺ to CH₂⁺ compared with CH₄⁺ giving CH₃⁺ is 0.19 and the value of Melton and Rosenstock is 0.16. Our value of approximately 2×10^{-16} cm.² for the cross section of the collision-induced decomposition of CH₄⁺ to CH₃⁺ is the same as their value of about 1×10^{-16} cm.² for ions accelerated through a potential of 2100 v.

A noticeable change in cross section, obtained from the ratio of diffuse peak to parent peak, was found on increasing the ion-accelerating voltage from 1000 to 3000 v. The cross sections for all of the decompositions of CH₅⁺ increased with increasing energy by a factor of 2 to 3. The relative cross sections for different decompositions did not change in exactly the same fashion. $I_{11.4}/I_{13.2}$, $Q(\text{CH}_5^+ \rightarrow \text{CH}_2^+)/Q(\text{CH}_5^+ \rightarrow \text{CH}_3^+)$, increased with increasing ion energy, but the ratio $I_{13.2}/I_{14.9}$, $Q(\text{CH}_5^+ \rightarrow \text{CH}_3^+)/Q(\text{CH}_5^+ \rightarrow \text{CH}_4^+)$, decreased with increasing ion energy. Of the decompositions of C₂H₅⁺, that to C₂H₃⁺ remained substantially constant while the others increased by less than a factor of two with an increase in ion energy from 1000 to 3000 v.

Acknowledgment.—We wish to express our appreciation to Mr. W. C. Gieger who performed these experiments with his accustomed skill and to Mr. O. G. Weir for performing the calculations.

(14) See, for example, C. E. Melton and H. M. Rosenstock, *J. Chem. Phys.*, **26**, 568 (1957), who also list earlier work.