TABLE VII

MASS SPECTRA OF THE DEUTERIOETHANES

m/e	C_2D_6[a]	C_2HD_5	$C_2H_2D_4$ 1,1,2,2	$C_2H_2D_4$ 1,1,1,2	$C_2H_3D_3$ 1,1,1	$C_2H_3D_3$ 1,1,2	$C_2H_4D_2$ 1,1	$C_2H_4D_2$ 1,2	C_2H_5D	C_2H_6
36	8.63	0.22								
35		8.65	0.20	0.20						
34	7.31	2.46	8.38	9.00	0.22	0.22				
33		6.31	4.37	4.28	9.49	8.81	0.16	0.28		
32	53.0	22.3	12.7	7.03	5.60	5.81	6.56	9.25	0.22	
31		30.0	26.5	33.5	8.92	18.6	5.50	7.55	10.1	0.26
30	15.7	9.85	22.0	20.0	40.9	29.3	17.1	27.6	8.60	10.9
29		6.25	9.43	9.70	13.5	16.5	23.5	25.6	36.1	9.93
28	12.9	8.89	8.43	8.43	9.82	9.74	20.0	14.2	23.2	46.6
27		2.65	5.11	5.05	7.45	7.08	14.1	9.60	12.3	17.1
26	2.18	1.83	2.05	1.99	2.85	2.77	10.1	4.50	7.37	12.2
25		0.20	0.45	0.45	0.79	0.75	2.26	1.16	1.68	2.48
24	0.42	0.36	0.38	0.37	0.41	0.39	0.77	0.45	0.47	0.51

[a] Carbon-13 peaks are eliminated in this pattern but may be obtained by adding 2.2% of the following even numbered mass peak height to each odd numbered mass peak height.

The two independent values of the second methane bond energy obtained here are in very good agreement, ≥ 104 and 103 ± 6 kcal./mole, respectively. These values are also in accord with the most recent spectroscopic and thermochemical findings.[11,12] All the results combined suggest the following energy "ladder" for the bond energies in methane

$$D(CH_3\text{-}H) = 102 \text{ kcal./mole}$$

$$D(CH_2\text{-}H) = 105 \pm 3$$

$$D(CH\text{-}H) = 108 \pm 3$$

$$D(C\text{-}H) = 82.7$$

Acknowledgments.—The authors wish to express their thanks to the National Science Foundation and to the California Research Corporation for grants which made this research possible. One of us (JAB) expresses his appreciation to the National Science Foundation for Fellowships held during the course of this research.

Appendix A

The mass spectrometric breakdown patterns for the deuterioethanes in the mass range 24–36 are given in Table VII since they may not all be found in the literature and may be of use to others. The breakdown patterns for all but two of the ethanes were given by Quinn and Mohler,[28] but there is a large discrepancy between their spectrum reported for 1,1,1-ethane-d_3 and the one we obtained. Lyon and Levy have used the results reported below with success.[29] A communication from Dr. Ausloos of the National Bureau of Standards indicates that the breakdown pattern has been redetermined and agrees with ours.[30] However, he indicates that the data presented here and by Quinn and Mohler for 1,1-ethane-d_2 are in error because the samples contain ethylene as a contaminant. Using Dr. Ausloos' new data the breakdown pattern for this ethane differs greatly from 1,2-ethane-d_2 only at those mass peaks corresponding to the loss of H_2, HD or D_2, which is consistent with the results for ethanes -d_3 and -d_4. The breakdown patterns presented have been normalized on the basis that the total number of ions produced in this region of the mass spectrum by each isotopic ethane is the same. The figures given are percentages of this total appearing at each mass number.

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(28) E. I. Quinn and F. L. Mohler, *J. Res. Natl. Bureau Standards*, **65A**, 93 (1961).

(29) R. K. Lyon and D. Levy, *J. Am. Chem. Soc.*, **83**, 4290 (1961).

(30) P. Ausloos, private communication.

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS]

Consecutive Ion-molecule Reactions in Methane[1]

BY S. WEXLER AND N. JESSE

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Reactions of positive ions with methane molecules have been studied at pressures of up to a few tenths of a millimeter in the source chamber of a mass spectrometer. Evidence indicates that increasingly heavy ions are formed in a chain of consecutive reactions between ions and the methane molecules. Some specific chains of such reactions are suggested. The two secondary ions CH_5^+ and $C_2H_5^+$ account for more than 70% of the total ion intensity at higher CH_4 concentrations. Cross sections for the reaction of primary ions with CH_4 have been determined from the exponential attenuations of the intensities of the individual species with increasing gas concentration. Reaction cross sections of the principal secondary ions have been estimated from the concentration dependences of the intensities of the secondaries. The resulting cross sections of the primaries agree reasonably well with those determined elsewhere by different methods. The results of the measurements are correlated with the ionic mechanism proposed for the reactions occurring in the radiolysis of CH_4.

A. Introduction

In the proposed mechanisms of chemical reactions occurring in the radiolysis of gases, it has usually been assumed that the primary ions produced by electron ionization and/or the secondary ions formed in the reactions of the primaries with the gas are neutralized by electron capture, and that the resulting free radicals then react to form

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

some of the observed products.[2–4] In illustration, Meisels, Hamill and Williams[2] propose that the secondary ions CH_5^+, $C_2H_5^+$ and $C_2H_7^+$ formed by reactions of primary ions with CH_4 are important intermediates in the radiation chemistry of methane which are neutralized by electron capture. Since neutralization is a relatively slow process,[5] the obvious assumption made is that these secondaries are very unreactive with CH_4 and therefore remain until they encounter free electrons. In addition, yields of radiolytic products have been calculated[3,4] from mass spectrometric data on primary ion abundances and reactions of the primaries with the parent molecule. These computations have ignored contributions to product yields from further ion-molecule reactions of the secondaries and of higher order species.

In most previous experiments[6] the study of the reactivity of secondary ions was precluded by the requirement of a relatively high pressure in the source at the same time as a good vacuum was demanded through the mass analyzer. To overcome these limitations Melton and Rudolph[7] employed a Po^{208} alpha ionization source and strong differential pumping to study ion-molecule reactions in the pressure range from 0.01 to 0.11 mm. These authors observed tertiary ions in ethylene and acetylene. More recently, Melton[8] has described experiments with cyanogen and xenon in which the pressure was as high as 1.0 mm. and ionization was effected by a beam of electrons. In addition, a quantitative mass spectrometric investigation of consecutive ion–molecule reactions in ethylene at pressures of tenths of a millimeter recently has been published by Field.[9] However, his approaches, both theoretical and experimental, differ from those presented here. This paper concerns itself with ionic reactions that occur in methane at pressures up to 0.4 mm. in the source chamber of a mass spectrometer which has very high differential pumping and produces ions by electron impact. The reactivities of primary and secondary ions may be determined quantitatively by measurements in this pressure region, and the reactions of higher polymeric species may also be studied.

B. Experimental

The mass spectrometer used in these investigations is a conventional one with a 60° magnetic sector of 12-in. radius of curvature with single directional focusing. Its distinguishing features are three 450 liter/sec. mercury diffusion pumps and large traps connected to the spectrometer through short tubes of 5 in. diameter, and a scintillation ion detector which counts individual ions, so that very weak electron beams can be used. The great pumping speed produced sharp decreases in pressure between the source chamber and other compartments of the mass spectrometer. In a typical experiment, when the pressure of CH_4 in the source was 0.17 mm., that in the chamber surrounding the source was 1.6×10^{-5} mm., while the pressure in the tube was 2×10^{-6} mm. The ionizing current of electrons, from a hot tungsten filament, enters the source chamber through a hole 0.025 mm. in diameter; and the positive ions leave through a slot 2.0 × 0.025 mm. A hemicylindrical electrode established a repeller field of 12.6 v./cm. to impel the ions toward the exit slit. The mean distance between the electron beam and the exit slit is estimated to be 3.2 mm. The temperature of the source chamber was observed to be 120 ± 3°.

The gas entered the source through large-diameter tubes from an 11.4 liter reservoir. Pressures of methane in the source chamber were determined from the pressures (measured with a McLeod gauge) in the reservoir and the rate of gas flow (calculated by use of Dushman's equation for viscous flow[10]) in the inlet system. Actually, the difference between the two values for the pressure was less than 2%.

Phillips research-grade CH_4 (99.60%) was further purified by passage through a Linde molecular sieve, according to the directions of Yang and Gant.

C. Results

1. Evidence for Consecutive Ion–Molecule Reactions.

—The mass pattern obtained by electron impact on CH_4 at relatively high source pressures is very different from that at very low pressures. At about 10^{-6} mm. in the source chamber, only the parent CH_4^+ ion and its unimolecular dissociation products (CH_3^+, CH_2^+, CH^+, C^+, H_2^+, and H^+) are observed. In contrast, the mass spectrum at the higher gas densities is very broad and complex. At a source pressure of 0.20 mm. (and with an ionizing beam of 140 v. electrons), for example, the intensities (relative to CH_4^+) of the positive

TABLE I

MASS SPECTRUM OF CH_4 AT A SOURCE PRESSURE OF 0.20 MM.

m/e	Probable species	Relative intensity[a]	m/e	Probable species	Relative intensity[a]
12	C	3	55	C_4H_7	19
13	CH	5	56	C_4H_8	6
14	CH_2	43	57	C_4H_9	31
15	CH_3	385	58	C_4H_{10}	5
16	CH_4	100	60	C_5	1.4
17	CH_5	16,000	61	C_5H	11
25	C_2H	11	63	C_5H_3	0.8
26	C_2H_2	39	65	C_5H_5	2
27	C_2H_3	5510	67	C_5H_7	1
28	C_2H_4	2450	69	C_5H_9	6
29	C_2H_5	19,150	71	C_5H_{11}	6
30	C_2H_6	586	73	C_6H	8
31	C_2H_7	129	75	C_6H_3	1.4
39	C_3H_3	159	76	C_6H_4	0.2
40	C_3H_4	207	77	C_6H_5	.3
41	C_3H_5	3690	79	C_6H_7	.8
42	C_3H_6	20	81	C_6H_9	1.4
43	C_3H_7	300	83	C_6H_{11}	3
44	C_3H_8	141	85	C_7H	6
45	C_3H_9	31	87	C_7H_3	3
47	C_3H_{11}	11	89	C_7H_5	0.6
51	C_4H_3	14	91	C_7H_7	0.6
53	C_4H_5	8	93	C_7H_9	1.5
			95	C_7H_{11}	8

[a] The intensity of each species has been corrected for naturally occurring C^{13}.

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(2) G. G. Meisels, W. H. Hamill and R. R. Williams, Jr., *J. Phys. Chem.*, **61**, 1456 (1957).

(3) J. H. Futrell, *J. Am. Chem. Soc.*, **81**, 5921 (1959).

(4) L. M. Dorfman and M. C. Sauer, Jr., *J. Chem. Phys.*, **32**, 1886 (1960).

(5) D. P. Stevenson, *J. Phys. Chem.*, **61**, 1453 (1957).

(6) See the review of F. W. Lampe, J. L. Franklin and F. H. Field, *Progress in Reaction Kinetics*, **1**, 69 (1961).

(7) C. E. Melton and P. Rudolph, *J. Chem. Phys.*, **32**, 586 and 1128 (1960), and earlier papers.

(8) C. E. Melton, *ibid.*, **33**, 647 (1960); C. E. Melton and P. S. Rudolph, *ibid.*, **33**, 1594 (1960).

(9) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

(10) S. Dushman, "Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 85.

(11) K. Yang and P. S. Gant, private communication

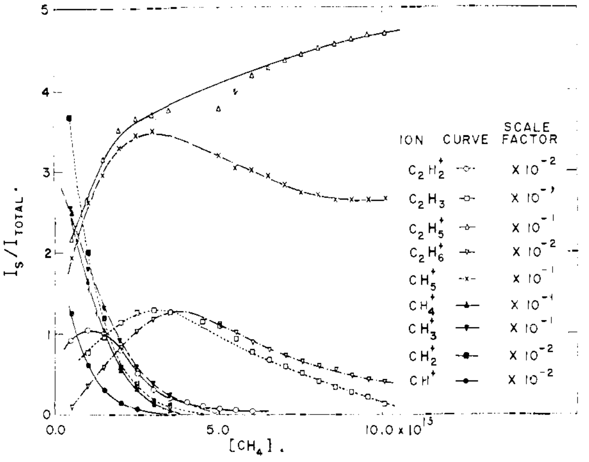

Fig. 1.—Variation with CH_4 concentration of normalized intensities of primary and secondary ions. The concentration of CH_4 is given in molecules per cm.^{3}. A concentration of 4.1 × 10^{16} molecules per cm.^{3} corresponds to a pressure of 0.20 mm. in the source chamber.

ions found are those given in Table I. It is seen that ions heavier than the parent often are much more abundant, *e.g.*, CH_5^+, $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$ and $C_3H_7^+$. Polymeric species containing up to seven carbon atoms were detected. Apparently, many of the ions are very reactive so that each successive ion interacts with the gas in the source chamber. With this density of methane in the source, the two ions CH_5^+ and $C_2H_5^+$ are extremely intense; they account for about 70% of the yield of all the ions.

The tabulated mass pattern is true only for the given pressure of methane, since the intensities of the ions vary in characteristic ways with increasing CH_4 concentration. In Fig. 1, the intensities of most of the primary and secondary ions from methane (expressed as fractions of the total intensity of all ions) are plotted as functions of the CH_4 concentration. In contrast to the primaries, whose intensity apparently decreases exponentially with gas density, the ionic products from the reactions of these species with CH_4 (*i.e.*, the secondary ions) increase rapidly and then usually decrease. The abundances of several molecular entities containing three carbon atoms also exhibit a rise, often followed by a drop-off, as the gas pressure increases (Fig. 2). These ions are apparently produced in reactions of secondaries with CH_4. The principal ionic products of further consecutive interactions are shown in Figs. 2 and 3. These are seen to be rising rapidly in the range of concentrations studied, although their relative abundances are still quite small. The behaviors of the ions show quite clearly that they are formed in chains of successive ion-molecule reactions and that the chains may be quite long, leading to a low degree of polymerization. The species observed do not appear to be the result of electron ionization of impurities in the methane. If they were, the normalized intensities of reactive ions would show an exponential decrease with pressure, similar to that of each primary ion (Fig. 1). And, if the ions were completely unreactive, the normalized intensity would be independent of the gas concentration in the source.

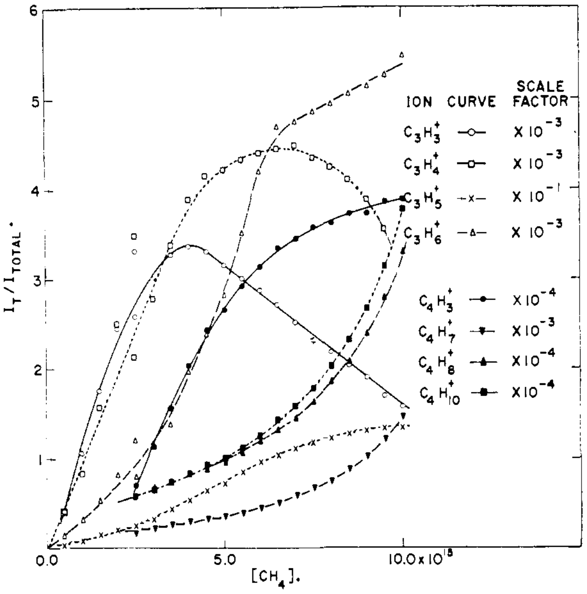

Fig. 2.—Dependences of the intensities of species containing three and four carbon atoms on density of CH_4 gas.

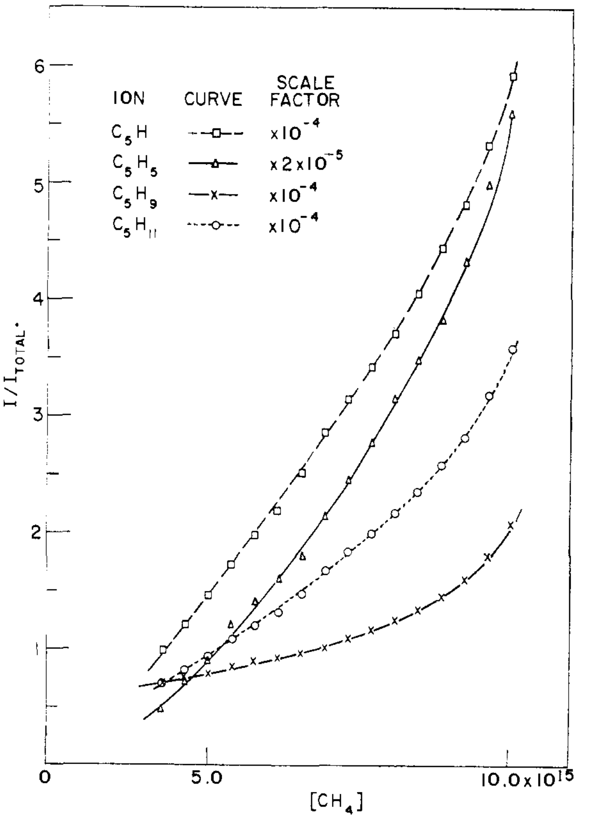

Fig. 3.—Intensities of ions containing five carbon atoms as a function of methane concentration.

The measured ion intensities were normalized by plotting the abundances as a function of methane concentration, summing the intensities of all ions at regular intervals of concentration, and calculating the ratios of ion intensity to total intensity at each of the source concentrations. This normal-

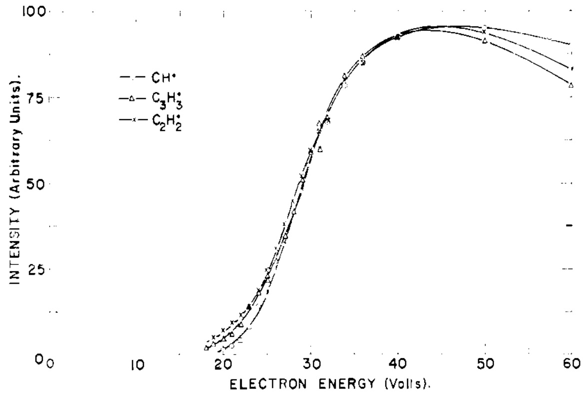

Fig. 4.—Ionization efficiency curves for the ions CH^+, $C_2H_2^+$ and $C_3H_3^+$ obtained in the high-pressure mass spectrum of methane.

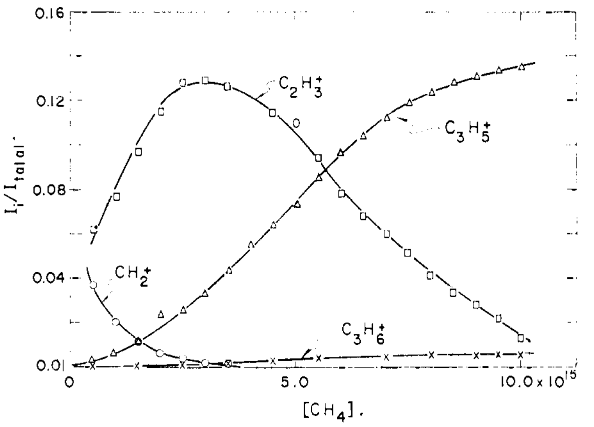

Fig. 5.—Relative intensities of ions in CH_2^+ chain of consecutive ion-molecule reactions *vs.* methane concentration.

izing procedure is necessary to ensure that the observed pressure dependences of the ion intensities are not affected by the fraction of molecules ionized or by differences in the efficiency of collection at different pressures, since the variation of total ion intensity with CH_4 concentration was observed to decrease linearly with increasing pressure above 0.10 mm. This, of course, is greatly different from the expected proportionality between the two variables. The experimentally observed relation is probably the result of attenuation of the electron beam as it crosses the source chamber to the critical region adjacent to the exit slit and of scattering of the ions at high gas densities.

Because of the rather complex mass pattern at high source pressures, data were collected over many days and fitted together to give the curves presented. The scatter of the results on ion intensities sometimes tends to produce irregularities in the plots, the most prominent being that in the normalized curve for $C_2H_5^+$.

Additional evidence for the consecutive nature of these ion-molecule reactions is derived from the appearance of the graphs of the different sequences of reactions and from measurements of appearance potentials, as described below.

2. Determination of Mechanisms of Consecutive Ion–Molecule Reactions.—The results presented above indicate that the ions formed in the methane react with the bulk gas in consecutive fashion. It is, of course, desirable to separate the large number of observed species into sets, each representing ions involved in a chain of consecutive reactions with CH_4. One method, extensively used to establish primary-secondary ion pairs, is the measurement of appearance potentials. The appearance potential of an ion formed in the reaction of a precursor ion with the gas should be the same as that of the reacting species. We have used this type of measurement to arrive at the set of ions involved in each chain of consecutive reactions. Representative results on ionization-efficiency curves appear in Fig. 4. These data were obtained when the pressure in the source was in the range from 0.070 to 0.12 mm. Electron scattering at these relatively high gas pressures probably accounts for the sometimes broad tails of the curves. We have therefore used the linear-extrapolation method to arrive at appearance potentials of the various ionic species. Despite the crudeness of these ionization-efficiency curves and the spread in appearance potentials, it was possible to separate the more prominent species into sets, each composed of ions in a particular chain of consecutive ion-molecule reactions (Table II). The assignment of polymeric species to one of four primary precursors is helped by the relatively large differences between appearance potentials of the primaries from CH_4. Incidentally, the correspondence of the appearance potential of the polymeric ion to that of one of the primaries from methane is additional evidence that the species of higher mass is derived from the primary and not from an impurity in the gas.

TABLE II

SETS OF IONS INVOLVED IN CHAINS OF CONSECUTIVE ION-MOLECULE REACTIONS IN CH_4

Primary ion	Intermediate ions
CH_4^+	CH_5^+, $C_2H_6^+$, $C_3H_8^+$, $C_4H_8^+$, $C_4H_9^+$
CH_3^+	$C_2H_4^+$, $C_2H_5^+$, $C_2H_7^+$, $C_3H_7^+$, $C_4H_7^+$, $C_5H_9^+$, $C_5H_{11}^+$
CH_2^+	$C_2H_3^+$, $C_3H_5^+$, $C_3H_6^+$
CH^+	$C_2H_2^+$, $C_3H_3^+$, $C_3H_4^+$

A well-known requirement for observing an ion-molecule reaction in the mass spectrometer is that the reaction not be endoergic. Calculations based on heats of formation of ions[12] and neutral species show this to be the case (within an estimated experimental error of about 25 kcal.) for all but one of the reactions leading to the intermediates listed in Table II. The exception is the reaction $CH_3^+ + CH_4 \rightarrow C_2H_4^+ + H_2 + H$, which is found to require 62 kcal./mole. Possibly, C_2H_4 is formed from reaction of an excited CH_4^+ with methane, so that the appearance potential of $C_2H_4^+$ appears to fall on that of the CH_3^+ species.

Using the sets indicated by the measurements of appearance potentials, we have combined the curves of fractional intensity *vs.* concentration (Figs. 1–3) of the ions in each sequence in order to visualize some characteristics of the consecutive reactions. For illustration, the combination of

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(12) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 243.

relative yield curves of the sequences starting with the primary ion CH_2^+ is shown in Fig. 5. One notes that the primary ion decreases roughly exponentially, the secondary ion rises and then decreases, and the tertiary ion is increasing in intensity in the range of gas concentrations studied. Similar figures are obtained for the other chains of ions. The forms and relative positions of the curves in each sequence remind one of the time variations of the intensities of nuclides involved in consecutive radioactive decay[13] and indeed is evidence that the ions react in consecutive fashion with CH_4. But our case is made more involved by competitive reactions of a given ion with CH_4. If species of low yield were included, the picture would undoubtedly be greatly complicated. It is of interest to note that the forms of these curves are very similar to those found with the α-ionization source,[7] despite the fact that in the latter the ionization is over a rather large, ill-defined volume, while in our experiment it is confined to a fairly well-defined cylindrical volume at a reasonably known distance from the exit slit.

An ionic mechanism for the reactions occurring in the radiolysis of methane, in which the species $C_2H_7^+$ is an important intermediate in the formation of some of the products, has been proposed by Meisels, Hamill and Williams.[2] They state that this ion is formed in an excited state as a collision complex of CH_3^+ and CH_4 and that the excitation is removed by collision with methane molecules. We have found this species ($m/e = 31$ in Table I) and have observed that its behavior with increasing CH_4 concentration differs from that of other supposedly secondary ions (Fig. 6). The increase in the intensity of $C_2H_7^+$ while the abundances of other secondary ions are decreasing may be due to collision stabilization of this species, as Meisels, *et al.*, have suggested. Also, the appearance potential of this species falls on that for CH_3^+, which suggests that CH_3^+ is indeed the precursor of the $C_2H_7^+$ ion.

3. Determination of Reaction Cross Sections.—For the evaluation of cross sections and reaction rates for the interaction of ions with neutral molecules in the source chamber of a mass spectrometer, Lampe, Franklin and Field[6] have developed a model based on steady-state concentrations of collision complexes. We prefer the alternative approach of looking at happenings in the source in terms of a "beam" of ions traveling from the region of electron ionization to the exit slit. As will be seen, the model advanced here, which can be considered to be an extension of the approach used for low-pressure measurements,[14] gives relations connecting ion intensities, gas concentrations and reaction cross sections which are similar to those developed from the "steady-state model." However, the "beam model" presents, we believe, a clearer physical picture of events in the source chamber.

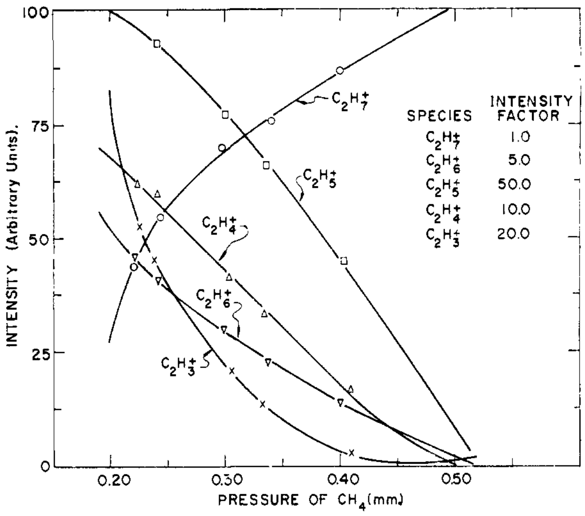

Fig. 6.—Variations of intensities of several secondary ions with increasing methane pressure in the source chamber of the mass spectrometer. The behavior of $C_2H_7^+$ is seen to contrast greatly with those of other secondary species.

If ions of a given primary species of intensity I_p^0 are generated at a distance d from the exit slit of the source chamber, the repeller field will urge them toward the slit. Reactions of the primary ions with the gas molecules will attenuate them in exponential fashion so that their intensity I_p at the exit slit will be given by

$$I_p = I_p^0 \exp\left[-\sigma_p^\tau[G]d\right] \qquad (1)$$

where σ_p^τ is the total cross section for reaction of the primary ion, $[G]$ the concentration of the gas and d the mean distance from the plane of origin of the primary ion to the exit slit.

Each species of secondary ions formed as products of the reactions of the primaries with the gas should also move toward the exit slit, this stream being also attenuated by interactions with neutral molecules. At any position x between the exit slit and the point of origin of the primary species which gives rise to the secondary species, the change of intensity of the secondary ions represents a balance between its increase by reaction of the primary and its decrease by its reaction with the gas, *i.e.*

$$\frac{dI_s}{dx} = \sigma_p[G] - \sigma_s^\tau[G] \qquad (2)$$

where σ_p is the partial cross section of the primary species for the reaction leading to the secondary ion of interest and σ_s^τ is the total reaction cross section of this secondary species. Integration between the proper limits yields

$$I_s = \frac{I_p^0\sigma_p}{\sigma_s^\tau - \sigma_p}\{\exp(-\sigma_p[G]d) - \exp(-\sigma_s^\tau[G]d)\} \qquad (3)$$

The differential equation for a particular tertiary species is similar to eq. 2, and the integrated form is

$$I_t = I_p^0\left[\frac{\sigma_p\sigma_s}{(\sigma_s - \sigma_p)(\sigma_t^\tau - \sigma_p)}\exp(-\sigma_p[G]d) + \frac{\sigma_p\sigma_s}{(\sigma_p - \sigma_s)(\sigma_t^\tau - \sigma_s)}\exp(-\sigma_s[G]d) + \frac{\sigma_p\sigma_s}{(\sigma_p - \sigma_t^\tau)(\sigma_s - \sigma_t^\tau)}\exp(-\sigma_t^\tau[G]d)\right] \qquad (4)$$

In eq. 4, σ_s is the partial cross section of the secondary ion for the reaction giving the tertiary ion of

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[13] E. Rutherford, J. Chadwick and C. D. Ellis, "Radiations from Radioactive Substances," Cambridge University Press, Cambridge, 1930, p. 12.

[14] D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955).

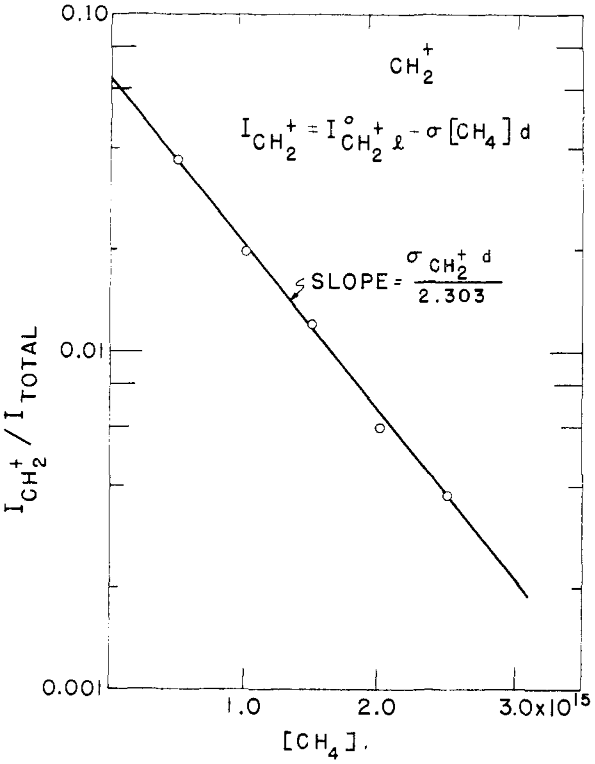

Fig. 7.—Semilogarithmic plot of the normalized intensity of CH_2^+ primary ion *vs.* CH_4 concentration.

interest, and σ_t^r is the total reaction cross section of the tertiary species. It should be apparent that eq. 1, 3 and 4 are completely analogous to the relations for the intensities of radioactive nuclides which form a chain in consecutive nuclear decay, with the reaction cross sections corresponding to the decay constants in the latter, and the product $[G]d$ corresponding to the time. Rutherford, Chadwick and Ellis[13] give relations that are applicable for representations of the variations of intensities of ions of higher order. Actually I_p^0, and therefore I_p, I_s and I_t in eqs. 1, 3 and 4, respectively, are functions of the degree of electron ionization and of the ion-collection efficiency. To compensate for these variations with source pressure, it is necessary to normalize the intensities of the ions as was described above. With the exception of a term in their relations, which reflects the reactivity of the intermediate complex, equations 1 and 3 developed here are seen to be identical with those presented by Lampe, *et al.*,[6] if cross section and distance are substituted for the reaction rate and time in their final relations. Their relation for tertiary ions differs from ours because of simplifying assumptions used in their treatment.

The exponential attenuation of the primary ions, given by eq. 1, appears to be confirmed by the behaviors of the ions CH_4^+, CH_3^+, CH_2^+ and CH^+ (Fig. 1). Since this is so, a semi-logarithmic plot of the normalized intensity against the gas concentration should be a straight line whose slope [from eq. 1] equals $\sigma_p^r d/2.303$. Accordingly, this treatment of the data should afford a means of determining the total cross sections for reaction of the primary ions with the neutral gas molecules. Such a plot of the intensity variation of the primary ion CH_2^+ is shown in Fig. 7. Good straight lines are obtained in the treatment of the data for CH_2^+ and CH^+, but the curves for CH_4^+ and CH_3^+ showed a slight downward curvature at the lowest CH_4 concentrations. The slope of the best straight line through the data is used to calculate the cross section σ_p^r for each primary species. These are listed in Table III. Variations in repeat measurements were at most 20%. The total reaction cross section of 39×10^{-16} cm.^{2}/molecule for CH_4^+, measured here for an electric field of 12.6 e.v./cm., may be compared with the values of 57×10^{-16} cm.^{2}/molecule determined by Field, *et al.*,[15] and 24×10^{-16} cm.^{2}/molecule inferred from the results of Tal'roze and Frankevich[16] for the specific reaction

TABLE III

CROSS SECTIONS FOR REACTIONS BETWEEN PRIMARY IONS AND CH_4

Primary ion	σ_p^r (10^{-16} cm.^{2} molecule^{-1})
CH_4^+	39
CH_3^+	27
CH_2^+	36
CH^+	45

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3$$

Also, our value of 27×10^{-16} cm.^{2}/molecule for the total cross section of CH_3^+ compares well with the value of 25×10^{-16} cm.^{2}/molecule, obtained by interpolation from the data of Schissler and Stevenson,[17] for the reaction

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

The results of the other investigators quoted here were derived from experiments performed at lower gas pressures in the source chamber and with different procedures.

Inspection of eq. 3 indicates that a plot of the logarithm of the normalized intensity of a secondary ion as a function of methane concentration should be linear at high values of the latter provided that $\sigma_p \neq \sigma_s^r$. If $\sigma_p > \sigma_s^r$, the slope of the linear portion should be $\sigma_s^r d/2.303$. These plots for the prominent secondary ions become approximately linear at high concentrations of CH_4, as illustrated by the curve for the secondary ion $C_2H_3^+$ in Fig. 8. The slopes of the linear portions imply the cross sections summarized in Table IV. Comparing the data in Tables III and IV, remembering the chains of consecutive ions listed in Table II, we may conclude that the values listed for CH_5^+, $C_2H_5^+$, and probably for $C_2H_3^+$ and $C_2H_2^+$, are indeed σ_s^r for these secondary species. Because the partial cross sections for reactions leading to the ions $C_2H_6^+$ and $C_2H_4^+$ are not known at present, the numbers listed in Table IV for these species may apply to reactivities of the primaries if $\sigma_p < \sigma_s^r$. Nevertheless, it is clear from this treatment of the intensity data that the cross sections for reaction

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

(16) V. L. Tal'roze and E. L. Frankevich, *J. Phys. Chem. USSR*, **34** (12), 1275 (1960) (translation).

(17) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

of secondary ions with methane are equal to or greater than the values listed in Table IV. It may therefore be concluded that, with the exception of the ion $C_2H_5^+$, the secondary ions also react with CH_4, some of them, on the first collision.

TABLE IV

CROSS SECTIONS FOR THE REACTIONS OF SECONDARY IONS WITH CH_4

Secondary ion	σ (10^{-16} cm.^{2} molecule^{-1})
CH_5^+	1.6
$C_2H_6^+$	6.0
$C_2H_5^+$	<0.1
$C_2H_4^+$	1.9
$C_2H_3^+$	10
$C_2H_2^+$	26

D. Discussion

To account for the main products of radiolysis of methane, Meisels, Hamill and Williams[2] have proposed two sequences of ionic reactions

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + CH_3 \quad (5)$$

$$CH_5^+ + e^- \longrightarrow CH_3 + H_2 \quad (6a)$$

$$\longrightarrow CH_2 + H_2 + H \quad (6b)$$

and

$$CH_3^+ + CH_4 \longrightarrow (C_2H_7^+)^* \quad (7a)$$

$$\longrightarrow C_2H_5^+ + H_2 \quad (7b)$$

$$(C_2H_7^+)^* + M \longrightarrow C_2H_7^+ \quad (8)$$

$$C_2H_7^+ + e^- \longrightarrow C_2H_6 + H_2 \quad (9a)$$

$$\longrightarrow C_2H_4 + H_2 + H \quad (9b)$$

$$C_2H_5^+ + e^- \longrightarrow C_2H_5 \quad (10a)$$

$$\longrightarrow C_2H_4 + H \quad (10b)$$

The free radicals CH_3 and C_2H_5 formed in the neutralization processes then react to give the observed products C_2H_6, C_3H_8, etc. Since neutralization by electron capture is a very slow process, being more than 10^6 times the time for ion-molecule reactions in gases at normal pressures,[5] it is clear that if the above sequences of reactions are valid, the ions CH_5^+, $C_2H_5^+$ and $C_2H_7^+$ must be very unreactive with methane molecules. In correlating our data with their scheme, it should be emphasized in advance that our results are from measurements on CH_4 at up to a few tenths of a millimeter pressure, while the radiolysis studies were performed at a pressure near one atmosphere. Acknowledging this limitation on the validity of the correlation, we find that our data in a limited way support the mechanism of Meisels, *et al.* The two species CH_5^+ and $C_2H_5^+$ dominate the mass pattern of CH_4 at relatively high source pressures, accounting for more than 70% of the total ion intensity. Further, the reaction cross section of $C_2H_5^+$ was so low as to be unmeasurable by the method used. Apparently, this ion is very inert and may remain until neutralized by the relatively slow processes of capture of a free electron or collision with the wall. But σ_s^r for CH_5^+, though small, appears to be large enough to remove these ions by reaction with CH_4 at normal pressures.

In Eqs. 7a and 8 we see that the foregoing investigators also propose that the reaction complex $C_2H_7^+$ from the interaction of CH_3^+ with methane is stabilized by collision with methane molecules at high pressure, and this ion is an important intermediate in the radiolysis of methane. We have indeed observed this species in low yield (Table I) in the higher part of the range of pressures we have studied (Fig. 6). Its interesting increase in intensity with rising CH_4 concentration in a pressure region where the abundances of other secondary ions are decreasing tends to support the suggestion of these workers that the $C_2H_7^+$ ion is stabilized by collision.

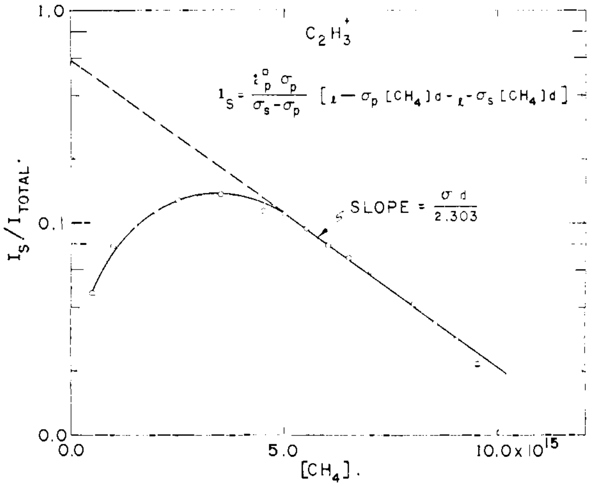

Fig. 8.—Semilogarithmic plot of normalized intensity of $C_2H_3^+$ secondary ion *vs.* CH_4 concentration.

Our results also may have a bearing on the molecular yield of hydrogen obtained in the radiolysis of methane. The molecular yield of H_2 measured on radiolysis agrees very well with that calculated by Dorfman and Sauer.[4] Their calculation is based solely on the relative abundances of the primary ions in electron impact on CH_4 in the mass spectrometer and the three ionic reactions

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \quad (11)$$

$$CH_5^+ + e^- \longrightarrow CH_3 + H_2 \quad (12)$$

and, in a minor degree

$$CH_4^+ \longrightarrow CH_2^+ + H_2 \quad (13)$$

It was tacitly assumed that other ion-molecule reactions contribute nothing to the yield of molecular hydrogen. In order that such good agreement between calculation and experiment be obtained, the $C_2H_5^+$ ion which is formed in reaction 11, and which accounts for almost half the yield in our experiments, must not give rise to H_2 on electron neutralization, for this would increase the yield by more than 45%. Therefore, it is likely that C_2H_5 (or more probably C_2H_4 + H) is the product of electron capture by $C_2H_5^+$, as suggested by Meisels, *et al.*[2] (eq. 10). Further, the apparent reactivity of CH_5^+ (Table IV) indicates that this ion is too short-lived to undergo electron capture (eq. 12). The shapes of the normalized intensity curves for CH_5^+ and $C_2H_5^+$ at higher methane concentrations (Fig. 2) suggest that CH_5^+ reacts with CH_4 to form $C_2H_5^+$. But we can think of no reaction by which this can occur that is not endoergic. From thermochemical considerations the most likely one is

$$CH_5^+ + CH_4 \longrightarrow C_2H_5^+ + 2H_2 \qquad (14)$$

which is endoergic by about 14 kcal./mole. It is possible, however, that the heat of reaction is zero or negative within the errors resulting from the uncertainties in measurements of appearance potentials, so that reaction 14 may indeed be energetically possible. But if we accept reactions 11 and 14, the calculated value of the molecular hydrogen yield per ion pair becomes 1.4, which is much larger than the experimental value of 0.9. And the value calculated should be a lower limit because molecular hydrogen is produced in most energetically favorable reactions between methane and ions other than $C_2H_5^+$ and CH_5^+. To complicate matters further, molecular H_2 is formed in the photolysis of CH_4.[18] Thus, one would expect the experimental molecular yield to be greater than that calculated by Dorfman and Sauer. But it leaves unexplained the agreement between calculated and observed yields of H_2 from CH_4 found by them and the disagreement we find.

Polymers, usually of unknown composition, have been found among the products of the radiolysis of methane.[2,19] Our observation of numerous polymeric ions, which appear to react in consecutive fashion with the gas, suggests that one plausible mechanism of the polymerization process in gaseous methane is just these rather long chains of ion-molecule reactions. The measurements on the reaction cross sections and the pressure dependences of the intensities of the various polymeric species indicate that many of these ions react quite readily.

Acknowledgments.—The authors wish to thank Professor W. H. Hamill and Dr. F. H. Field for their valuable comments on this paper.

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[18] B. H. Mahan and R. Mandel, *J. Chem. Phys.* (in press).

[19] R. W. Lampe, *J. Am. Chem. Soc.*, **79**, 1055 (1957).

[CONTRIBUTION FROM THE INTERNATIONAL BUSINESS MACHINES CORPORATION, THOMAS J. WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, NEW YORK]

Photoisomerization of 1,3,5-Cycloheptatriene and its Relation to Internal Conversion of Electronic Energy

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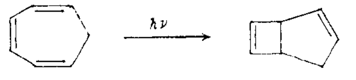
The photolysis of 1,3,5-cycloheptatriene in the vapor phase led to the formation of toluene and bicyclo[3.2.0]heptadiene-2,6. The quantum yield for toluene increased with decreasing pressure, the extrapolated value at zero pressure being unity within experimental error. Inert gases such as helium, xenon, methane, carbon dioxide, nitric oxide, oxygen and diethyl ether affected the quantum yield in qualitatively the same way as pure cycloheptatriene but quantitatively their efficiencies seemed to fall in the order of their boiling points and molecular weights. In particular, xenon seemed to be much more efficient than helium as a quencher. The quantum yield for the formation of bicycloheptadiene was also pressure dependent, although the effect was small and the yield increased with an increase in pressure. Under the most favorable conditions only 5% or less of the excited cycloheptatriene molecules isomerized this way. It is suggested that isomerization to toluene occurs not from an electronically excited molecule of cycloheptatriene but from a vibrationally excited ground state molecule that is formed by the internal conversion of the electronic energy. In contrast, the formation of bicycloheptadiene is believed to occur from electronically excited cycloheptatriene.

Introduction

The photolysis of 1,3,5-cycloheptatriene in diethyl ether solution has been studied by Dauben and Cargill.[1] The products they obtained were bicyclo[3.2.0]heptadiene-2,6, a small amount (2–5%) of toluene and a polymer. The formation of bicycloheptadiene from cycloheptatriene constitutes a photoisomerization reaction which resembles the photodimerization of olefins to give cyclobutane derivatives.



(1)

The present investigation of the photolysis of cycloheptatriene in the vapor phase was conducted as part of a program of study of the photochemistry of simple aliphatic dienes and trienes.[2] In particular, it was of interest to see if reaction 1 will occur in the vapor phase since neither 1,3-butadiene nor 1,3-cyclohexadiene has been observed to undergo analogous photoisomerization reactions.[2,3]

Experimental

Cycloheptatriene was obtained from the Chemical Procurement Laboratories (College Point 56, New York). It was fractionated on an 18″ spinning band column of 23 theoretical plates. A small constant boiling fraction was collected, dried and admitted to the vacuum line. It was degassed and stored at Dry Ice temperature. Analysis by vapor phase chromatography showed that it contained traces of toluene and bicyclo[2.2.1]heptadiene-2,5 as impurities. It was found that neither compound interfered with the course of the photolysis of cycloheptatriene but a 2–4% correction had to be applied to the toluene yield that was obtained experimentally.

The following gases of reagent grade purity were obtained in sealed glass bulbs and used as such: helium, xenon and methane (Linde Co.); oxygen and carbon dioxide (Airco). Nitric oxide (Matheson Co.) was distilled from −156 to −195° before use. The diethyl ether used was the best analytical grade that was available. It was degassed before use.

A conventional high vacuum line in which the cycloheptatriene did not come in contact with stopcock grease

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[1] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961). The sample of cycloheptatriene used by these workers contained a small amount of toluene. Since they have not reported if the toluene found at the end of the photolysis was more than what was initially present, it is not known if toluene is formed during photolysis in solution.

[2] R. Srinivasan, *J. Am. Chem. Soc.*, **82**, 5063 (1960); **83**, 2806 (1961).

[3] R. J. de Kock, N. G. Minnard, and E. Havinga, *Rec. trav. chim.*, **79**, 922 (1960).