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Reactions of Gaseous Ions. VIII. Multiple Order Ion–Molecule Reactions and the Ultra-High Pressure Mass Spectrum of Ethylene

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A study of the ion–molecule reactions occurring in ethylene at very high (up to 350 μ) ionization chamber pressures has been made. The mass spectrum of ethylene was determined at a pressure of 212 μ, and 46 ions produced by ion–molecule reactions, *i.e.*, those with mass greater than 28, are observed. The highest mass observed is 119, which corresponds to the ion $C_9H_{11}^+$. The most intense ion in the spectrum is $C_3H_5^+$ (mass 41), a secondary ion, and the most intense ion with kinetic order higher than two is $C_5H_9^+$ (mass 69). The product ions with mass above 69 are predominantly those which are most often observed in the mass spectra of aromatics, namely, $C_6H_5^+$, $C_6H_7^+$, $C_7H_7^+$, $C_8H_7^+$ and $C_8H_9^+$ (masses 77, 79, 91, 103 and 105). The primary ion spectrum is different from that observed at low pressures in that the relative intensity of the mass 26 ($C_2H_2^+$) ion is much lower at the high pressure. From acetylene–ethylene mixture studies the charge exchange reaction $C_2H_2^+ + C_2H_4 = C_2H_4^+ + C_2H_2$ is postulated, and the diminution of the $C_2H_2^+$ intensity in the high pressure ethylene spectrum is explained on the basis of the charge exchange process. The bimolecular rate constant for the charge exchange reaction is determined to be 4.1×10^{-10} cc./molecule sec. The primary ions which serve predominantly as reactant ions for the formation of several tertiary product ions have been identified. Including, for the sake of greater completeness, the secondary ions studied in previous work, it has been established that $C_2H_4 \rightarrow C_3H_5^+$, $C_4H_7^+$, $C_4H_8^+$ and $C_5H_9^+$; $C_2H_3^+ \rightarrow C_2H_5^+$, $C_5H_7^+$ and $C_6H_5^+$; $C_2H_2^+ \rightarrow C_3H_3^+$, $C_4H_5^+$, $C_4H_6^+$ (?), $C_5H_5^+$ and $C_6H_7^+$. Studies of the variation of ion intensity with ionization chamber pressure have been made for the more intense product ions. Pressures up to 350 μ were used. From these pressure studies the kinetic orders of the reactions evolving the product ions were deduced and for the second and third order reactions rate constants were determined. The third order rate constants here obtained are appreciably higher than the third order rate constants for the reactions of neutral species. The rate constant values obtained for six tertiary ions range from 1.5×10^{-27} to 7.6×10^{-27} cc.^{2}/molecule^2 sec. A kinetic model for the ionization chamber reactions is set up, and from it a mathematical description of the kinetics is derived. It is shown that the tertiary ions for which pressure studies are made can, with a good deal of certainty, be considered as formed from a sequence of two intermediate complex ions, and one then can express the third order rate constant in terms of two second order constants and a first-order constant. Making a reasonable assumption about the relationship between the second-order constants, experimental values can be obtained for the unimolecular decompositions of the second-order intermediate complexes formed in the ion-molecule reactions. The values obtained for the totality of the known decompositions of $C_4H_6^+$, $C_4H_7^+$ and $C_4H_8^+$ are: 1.0×10^7, 4.3×10^7 and 4.0×10^7 sec.$^{-1}$. Using these various values of the rate constants, curves for the variation of the ion intensities with pressure are calculated from the kinetic model. The agreement between calculated and experimental curves is good for 8 ions and poor for 3 ions. The kinetic orders of the reactions resulting in the product ions deduced from the pressure studies (and from stoichiometric considerations) range from 2 for the C_3–C_4 ions to 6 for $C_7H_{13}^+$ (mass 97). Several fifth order ions are found, as well as numerous fourth and third order ions. These high kinetic orders signify that we have succeeded in effecting a kind of low-order ionic polymerization in the gas phase.

The ion–molecule reactions occurring in ethylene were studied some time ago in this Laboratory.[1] The ionization chamber pressure range considered was approximately 0–20 microns, which in the mass spectrometer used for the studies was sufficient to give secondary ions with abundances as high as about 10% those of the most intense primary ions. Recently, Melton and Rudolph have reported[2] a study of the alpha-particle radiolysis of ethylene in an alpha-particle mass spectrometer. Pressures as high as 100 microns were used, and at the highest pressure the intensity of the secondary mass 41 ion ($C_3H_5^+$) was approximately twice that of the most intense primary ion. In addition, a tertiary ion of mass 69 ($C_5H_9^+$) was reported. The reactions postulated for the production of certain secondary ions were different from those postulated by us.[1]

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

[2] C. E. Melton and P. S. Rudolph, *J. Chem. Phys.*, **32**, 1128 (1960).

We wish to report in this paper a new study on ethylene at ionization chamber pressures up to 350 microns. It is our hope in this work to learn about the reactions and behavior of ions under conditions which more closely approximate the atmospheric pressure-condensed phase conditions of conventional chemical reactions than has so far been the case in mass spectrometer studies of ion–molecule reactions.

Experimental

All the measurements here reported have been made in a new mass spectrometer designed in these Laboratories as a general purpose instrument for chemical physics research. It is a 12" radius of curvature 60° magnetic deflection instrument with conventional means of producing, analyzing and collecting the ions.

The ability of the apparatus to operate at very high pressures is the consequence of the fact that it is fitted with a high capacity pumping system. The volume containing the ion source and the ion gun and the mass analyzer volume are separately evacuated by 300 liter/sec. oil diffusion pumps connected to the system through high conductance cold traps and the short (2 ft. in length), large (4 in. diameter) pipes. The only connection between the two volumes being evacuated is the last slit of the ion gun, the dimensions of which are 10 × 0.25 mm., and consequently a high pressure differential can be maintained between the two volumes. A fairly high differential pressure also can be maintained between the ionization chamber and the volume outside it. The highest source pressure at which the instrument has so far been operated is about 600 μ, which produced an analyzer pressure of about 8×10^{-6} mm. Even at this high pressure the mass spectral peaks are well defined and scattering effects are not significant.

The pressure of gas entering the mass spectrometer tube is determined by means of a McLeod gage connected to the ionization chamber gas inlet tube at a distance from the ionization chamber of about 15 inches. The pressure in the ionization chamber was determined by measuring the total ionization in ethylene, collecting the ions formed in the electron beam on the ion repellers. At the high source pressures involved in this study, it was necessary to make the bias on the repellers as large as −45 v. in order to achieve current saturation. Ion source pressures were calculated from the ion currents using the ionization cross-section for ethylene given by Lampe, Franklin and Field.[3] Total ionization currents were measured for various McLeod gage pressures up to about 900 microns, and a calibration relationship giving the ionization chamber pressure in terms of the McLeod gage pressures was constructed.

While we were confident from previous experience that this method of determining pressure is valid at relatively low pressures, we are concerned about its applicability at high pressures where a significant fraction of the incident ionizing electrons experience collisions with gas molecules. We calculate from the usual exponential attenuation equation that at a source pressure of 500 μ, only about 1% of the incident electrons pass through the source without collision, and it is reasonable to wonder whether the total ionization is a good measure of the source pressure. Consequently, as a check, semi-independent determinations of the source pressure from gas flow considerations were made. The gas flow rate at various inlet tube pressures (measured by the McLeod gage) was determined by measuring the time rate of pressure diminution in the reservoir (of known volume) upstream from the gold foil molecular leak. If we could have determined exactly the length of the radius of the tube from the McLeod gage to the ion source, the pressure drop in the tube could have been calculated and a completely independent determination of source pressure thus effected. However, the radius of the tube is not constant, and it would have been impractical to attempt to measure the various radii with the degree of accuracy necessary to make meaningful calculations.

The gas flow in the pressure range in which we are interested is intermediate between laminar flow and molecular flow, and from the discussions and equations given by Dushman[4] it may be concluded that to a satisfactory approximation the source pressure (P_s) is a quadratic function of the inlet line manometer pressure (P_m). Thus we have

$$k/2\,P_s^2 + CP_s = k/2\,P_m^2 + CP_m - F \qquad (1)$$

where F is the experimentally determined flow rate, and C and k are empirical constants. The constants C and k were evaluated from two sets of values of P_m, F and P_s, where the latter quantity was determined by total ionization measurements and the pressures chosen were those for which total ionization measurements are known to be valid, *i.e.*, low pressures ($P_s < 40\ \mu$).

The P_s–P_m relationship determined from total ionization measurements was in excellent agreement with that determined from flow rate measurements (calculated from eq. 1), and we believe that the relative accuracy of one P_s value with another is in the range 1–5%. The absolute accuracy of the P_s values is limited by the absolute accuracy of the ethylene ionization cross-section used, the absolute accuracy of ion collection, and by the accuracy with which the temperature of the ionization chamber is known. However, uncertainties in ionization chamber temperature will not affect the rate constants given in this work, since these quantities are expressed in terms of numbers of molecules per unit volume which is the quantity yielded directly by the total ionization measurements.

The instrumental operating conditions generally used to obtain the data reported on this paper are as follows. Ionizing current = 0.1 to 0.3 μamp. measured with a vacuum tube millimicroammeter. For some studies of low intensity, high kinetic order ions an ionizing current of 6.0 μamp. was used. The applied ionizing voltage was 100 v., and 5.0 v. was applied to the ion repeller electrodes. Since the distance between the repellers and the ion-exit electrode is 4.0 mm., this repeller voltage corresponds to an ionization chamber field strength of 12.5 v./cm. The ion accelerating voltage was 2000 v., which is about the maximum voltage which could be applied without the occurrence of arcs at the highest pressures of ethylene. The whole mass spectrometer tube except for the ion collector chamber was heated to 150–200°. It is to be regretted that the design of the ion source thermocouple is faulty, and we do not have accurate measurements of the source temperature. However, from the known source envelope temperature, the readings (admittedly somewhat faulty) of the source thermocouple, and an estimate of the temperature rise caused by the filament, we estimated the source temperature to be 200°, and we doubt seriously that this estimate is in error by more than 25°. Ion currents were measured with an Applied Physics Corp. Model 36 vibrating reed electrometer. In this paper ion currents are expressed in terms of chart divisions, where nominally 1 chart division = 1×10^{-15} amp.

The ethylene used in this work was Phillips Research Grade, which has a stated purity of 99.9%. In addition, it was subjected to analysis by gas chromatography, which yielded as impurities in p.p.m.: CH_4, 3, C_3H_8, 7, *i*-C_4H_{10}, 1, and CO_2, 1. A special effort was made to look for impurities of relatively high molecular weight (above 60), which in the mass spectrometer would yield ions which might be confused with those produced by high order ion–molecule reactions. None was found.

Results

Mass Spectra.—The mass spectrum of C_2H_4 at an ion source pressure of 212 μ is given in Table I. Two values of the electron current were used to measure the very wide range of ion intensities found. The ions with mass 84 and less were observed with an electron current of 0.1 μamp., whereas those with mass above 84 were observed with an electron current of 6.0 μamp. For the preparation of Table I, the intensities of the latter group of ions was divided by 60 so as to make them directly comparable with those of the first group. The ion current–electron current linearity is such as to make the procedure valid.

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[3] F. W. Lampe, J. L. Franklin and F. H. Field, *J. Am. Chem. Soc.*, **79**, 6129 (1957).

[4] S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 111 ff.

TABLE I

MASS SPECTRUM OF C_2H_4[a]; $P_s = 212\ \mu$

Mass	Formula[b]	Intensity (divisions)	Mass	Formula[b]	Intensity (divisions)
24 + 24.1	C_2^+	185	67	$C_5H_7^+$	480
25	C_2H^+	120	69	$C_5H_9^+$	1750
26	$C_2H_2^+$	780	71	$C_5H_{11}^+$	3
27	$C_2H_3^+$	6400	75	$C_6H_3^+$	14
28	$C_2H_4^+$	11800	76	$C_6H_4^+$	9
29	$C_2H_5^+$	16100	77	$C_6H_5^+$	135
30	$C_2H_6^+$	111	78	$C_6H_6^+$	16
37	C_3H^+	30	79	$C_6H_7^+$	147
38	$C_3H_2^+$	360	81	$C_6H_9^+$	6
39	$C_3H_3^+$	3530	82	$C_6H_{10}^+$	2
40	$C_3H_4^+$	980	83	$C_6H_{11}^+$	40
41	$C_3H_5^+$	43300	84	$C_6H_{12}^+$	4
43	$C_3H_7^+$	117	85	$C_6H_{13}^+$	0.56
50	$C_4H_2^+$	50	89	$C_7H_5^+$	0.08
51	$C_4H_3^+$	378	91	$C_7H_7^+$	6.4
52	$C_4H_4^+$	405	93	$C_7H_9^+$	0.30
53	$C_4H_5^+$	2500	95	$C_7H_{11}^+$	0.08
54	$C_4H_6^+$	236	97	$C_7H_{13}^+$	2.8
55	$C_4H_7^+$	3510	99	$C_7H_{15}^+$	0.08
56	$C_4H_8^+$	1266	103	$C_8H_7^+$	7.7
57	$C_4H_9^+$	162	105	$C_8H_9^+$	5.3
62	$C_5H_2^+$	1	107	$C_8H_{11}^+$	0.15
63	$C_5H_3^+$	42	111	$C_8H_{15}^+$	.05
64	$C_5H_4^+$	5	112	$C_8H_{16}^+$	.10
65	$C_5H_5^+$	162	119	$C_9H_{11}^+$	.05
66	$C_5H_6^+$	23			

[a] Intensities tabulated for ions of mass 85 and above obtained by multiplying experimentally observed intensities by 1/60 to take into account a difference in magnitude of ionizing current. [b] Intensity at mass number $C_nH_m^+$ corrected for contribution of $^{13}CC_{n-1}H_{m-1}^+$ if latter is 10% or more of total. Correction made assuming that abundance of ^{13}C is 1.1%.

From studies of the pressure–intensity relationships for the more intense ions in Table I and from the high purity of the ethylene used, we are of the opinion that the ions of mass greater than 28 are the products of gas phase ion–molecule reactions in ethylene. The mass 41 ($C_3H_5^+$) ion is the most intense in the mass spectrum, and even the mass 29 ion is more intense than the primary ions. The mass 69 ($C_5H_9^+$) ion is the most intense of the higher mass (and kinetic order) ions, and this ion also has been observed in the mass spectrum of ethylene by Melton and Rudolph.[2] The highest mass ion observed is $C_9H_{11}^+$ (mass 119), which from stoichiometry must involve as a minimum for its formation the participation of 5 ethylene (C_2) entities. Thus a kind of low order gas phase ionic polymerization has been effected. A preponderence of the rather large variety of ions formed contain an odd number of H-atoms, and those ions which do contain an even number of H-atoms are formed in relatively small abundances. In the ion groups containing six or more carbon atoms, the mass of the most intense ion (or ions) at each carbon number is a mass which is generally found (usually with greatest intensity) in the mass spectra of aromatic compounds, *viz.*, masses 77, 91, 105 and 119 (homologous series $C_nH_{2n-7}^+$). We also include in this list mass 79 ($C_6H_7^+$, protonated benzene) and mass 103 ($C_8H_7^+$, largest fragment ion from styrene). We tentatively postulate that the ions formed at these masses by reactions in ethylene are aromatic fragment ions. It is to be noted that with the exception of a small intensity at mass 78 the corresponding aromatic parent ions are completely absent. Clearly, the observed ions are not formed from aromatic molecules produced from the ethylene by neutral molecule processes.

It is of interest that the secondary ions found in 1,3-butadiene by Barker, Hamill and Williams[5] are to a considerable extent the same as those we find in ethylene. Thus, the masses of the five most intense butadiene secondary ions are (in order of decreasing magnitude): 77, 65, 79, 91 and 80. Only the ion of mass 80 does not appear in the ethylene spectrum.

The relative intensities of the mass 24–28 ions (primary ions) found in Table I are quite different from those found in conventional, low-pressure mass spectra (ions formed solely by first order processes). At low pressures, the mass 26 and 27 intensities are both about 60% of the mass 28 intensity. From Table I, one calculates that the intensity of 27 is 54% of the 28 intensity, not a great change; but the mass 26 relative intensity is 7%, *i.e.*, lower by a factor of about 10. A similar calculation gives the result that the mass 25 intensity also decreases by about a factor of 10. There are two possible explanations for the intensity diminution of the mass 26 ion (to which we shall restrict our remarks). Namely, with the increase in pressure. the mass 26 ion undergoes more reactions than the mass 27 or 28 ions, or, on the other hand, the increase in pressure somehow inhibits the formation of the mass 26 ion from the parent ion.

We can show that the mass 26 ion does not undergo appreciably more extensive conventional, condensation-type ion molecule reactions than do the mass 27 or mass 28 ions in the following way. From the previous study on ethylene[1] and from experiments to be described later, the reactions producing the major ions found in the high pressure spectrum of ethylene are reasonably well known. The mass 26, 27 and 28 ions are the major primary ions in the ethylene mass spectrum, and each ion acts as a precursor for a group of product ions, which may be formed either directly from the primary ion or as a result of a sequence of reactions. The ions known to be formed by conventional ion-molecule reactions from each primary ion are

$$28(C_2H_4^+) \longrightarrow 41(C_3H_5^+) + 55(C_4H_7^+) + 56(C_4H_8^+) + 69(C_5H_9^+) \quad (2)$$

$$27(C_2H_3^+) \longrightarrow 29(C_2H_5^+) + 67(C_5H_7^+) + 77(C_6H_5^+) \quad (3)$$

$$26(C_2H_2^+) \longrightarrow 39(C_3H_3^+) + 53(C_4H_5^+) + 54(C_4H_6^+) + 65(C_5H_5^+) + 79(C_6H_7^+) \quad (4)$$

Thus, we may write for the initial intensity (I_m^0) of the ion of mass m, that is, the intensity immediately after ion formation in the electron beam and before any ion-molecule reactions have occurred

$$I_{28}^0 = I_{28} + I_{41} + I_{55} + I_{56} + I_{69} \quad (5)$$

$$I_{27}^0 = I_{27} + I_{29} + I_{67} + I_{77} \quad (6)$$

$$I_{26}^0 = I_{26} + I_{39} + I_{53} + I_{54} + I_{65} + I_{79} \quad (7)$$

From Table I, we calculate the following values: I_{28}^0 = 61,600 div., I_{27}^0 = 23,100 div., I_{26}^0 = 7,350

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

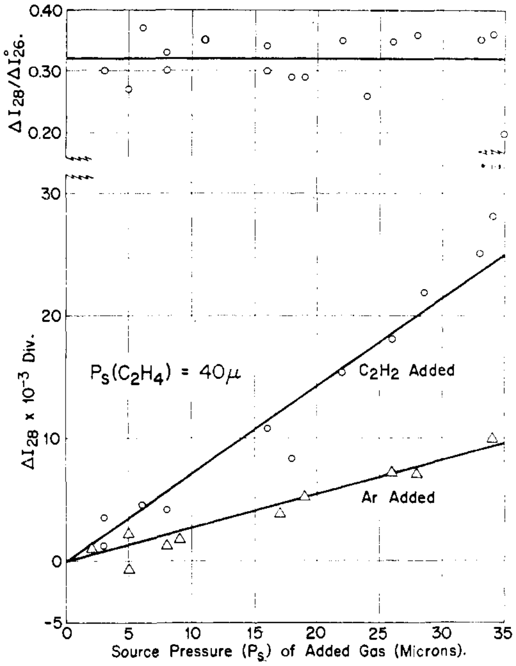

Fig. 1.—$C_2H_2^+$–C_2H_4 charge exchange experiment.

div., $I_{27}^0/I_{28}^0 = 0.38$, $I_{26}^0/I_{28}^0 \doteq 0.12$. The agreement between the values for I_{26}^0/I_{28}^0 and I_{26}/I_{28} is good enough to indicate that at best only a small part of the decrease in the relative intensity of mass 26 can be attributed to the formation of the product ions given in eq. 2–4.

$C_2H_2^+$–C_2H_4 Charge Exchange.—However, we have observed evidence for a reaction between $C_2H_2^+$ and C_2H_4, namely, charge exchange, which we think does constitute the basis of a reasonable explanation for the change in the ethylene mass spectrum with pressure. We have found that the addition of acetylene to ethylene in the mass spectrometer results in an increase in the mass 28 ($C_2H_4^+$) intensity, as is represented in the bottom portion of Fig. 1. Ethylene in an amount sufficient to give a source presure of 40 μ was introduced into one of the two gas handling reservoirs, and variable amounts of acetylene (Matheson, 99.5% minimum purity, passed through a CO_2–methanol trap to remove acetone) were introduced into the other gas handling reservoir. The largest amount of acetylene used gave roughly equal concentrations of ethylene and acetylene. In Fig. 1 ΔI_{28}, the change in the mass 28 intensity brought about by the addition of acetylene is seen to increase linearly with acetylene pressure. This increase could be the result of some trivial experimental effect such as, for example, an enhancement of the flow rate of ethylene by the acetylene. To investigate this, we repeated the experiment using argon as the added gas. As may be seen in Fig. 2, some increase in the mass 28 intensity occurred but to a smaller extent than with acetylene. We interpret the increase in the mass 28 intensity when acetylene is added as evidence for the occurrence of the charge exchange reaction

$$C_2H_2^+ + C_2H_4 = C_2H_4^+ + C_2H_2 \qquad (8)$$

Since the acetylene concentration is kept smaller than the ethylene concentration, a constant relationship should exist between the change in the $C_2H_4^+$ concentration when acetylene is added (represented by ΔI_{28}) and the change in the initial $C_2H_2^+$ concentration (represented by ΔI_{26}^0). In this case ΔI_{26}^0 was calculated from the relationship

$$\Delta I_{26}^0 = \Delta(I_{26} + I_{39} + I_{53} + I_{54} + I_{28}) \qquad (9)$$

and the values of the ratios $\Delta I_{28}/\Delta I_{26}^0$ for the several acetylene pressures are plotted in the upper portion of Fig. 1. These points were obtained in three different experiments, in one of which the ion source operating conditions were quite different from those obtaining in the other two, and the excellent constancy of the ratio supports the postulate of charge exchange.

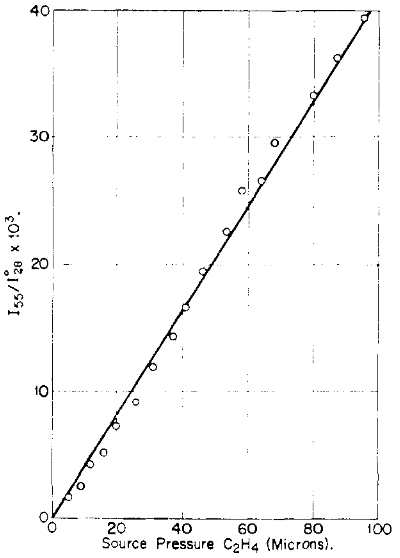

Fig. 2.—I_{55}/I_{28}^0 *vs.* C_2H_4 source pressure.

The kinetics for the charge exchange reaction 8 can be written as follows. The ion concentrations referred to are those involved in the charge exchange reaction. The ethylene concentration is taken as a constant.

$$-\frac{d[C_2H_2^+]}{dt} = k_8[C_2H_2^+][C_2H_4] \qquad (10)$$

The integration is carried over $\tau_{C_2H_2^+}$, the residence time of $C_2H_2^+$ in the ion source

$$\ln\frac{[C_2H_2^+]}{[C_2H_2^+]_0} = -k_8[C_2H_4]\tau_{C_2H_2^+}$$

But

$$[C_2H_4^+] = [C_2H_2^+]_0 - [C_2H_2^+]$$

so

$$\ln\left(1 - \frac{[C_2H_4^+]}{[C_2H_2^+]_0}\right) = -k_8[C_2H_4]\tau_{C_2H_2^+} \qquad (11)$$

Taking $[C_2H_4^+]/[C_2H_2^+]_0$ to be 0.32, the average value of $\Delta I_{28}/\Delta I_{26}^0$ calculated from Fig. 1, $\tau_{C_2H_2^+} = 9.26 \times 10^{-7}$ sec., calculated from the voltage applied to the ion repeller and the source dimensions, and $[C_2H_4] = 8.0 \times 10^{-14}$ molecules/cc. corresponding to $P_s = 40\ \mu$, we calculate from eq. 11 the value 4.1×10^{-10} cc./mol. sec. for k_8, the rate constant for the charge exchange reaction. This value is of the order of magnitude usually found for ion–molecule reactions.

We now use this reaction rate constant in explaining the diminution of the relative intensity of the mass 26 ($C_2H_2^+$) ion in the high pressure mass spectrum of ethylene. The standard attenuation equation may be written $I/I_0 = \exp(-Nk\tau)$, and if we apply this equation to the attenuation of the mass 26 ion at an ethylene pressure of 212 μ (the pressure of Table I), we obtain $I/I_0 = 0.20$. Again, we assume for simplicity that the decomposition of ethylene under electron impact is such as to give mass 26 and 27 ions with intensities 60% that of the mass 28 ion. However, before the ions leave the ionization chamber, 80% of the mass 26 ions are neutralized in a charge exchange process which produces mass 28 ions. The relative intensities of the ion currents at masses 26, 27 and 28 are

$$\frac{I_{26}}{I_{28}} = \frac{0.60 \times 0.20}{1 + 0.80 \times 0.60} = 0.081,$$

$$\frac{I_{27}}{I_{28}} = \frac{0.60}{1 + 0.80 \times 0.60} = 0.41 \qquad (12)$$

These relative intensities are remarkably close to the experimental values of I_{26}^0/I_{28}^0 and I_{27}^0/I_{28}^0 (0.12 and 0.38, respectively) calculated from Table I, and the agreement provides support for the postulate that acetylene ion undergoes charge exchange with ethylene.

Unfortunately our conclusion concerning the occurrence of charge exchange between acetylene ion and ethylene is exactly the opposite of that of Rudolph and Melton,[6] who from studies of the alpha radiolysis in a mass spectrometer of ethylene, acetylene and a mixture of the two reach the conclusion that no charge exchange occurs. On the other hand, from a similar experiment with acetylene and benzene, they decide that charge exchange does occur in this system.

They obtain the spectrum of ethylene alone and in the presence of a tenfold excess of acetylene ($P(C_2H_4) = 0.1$ mm.), and they find that the mass 28 + mass 41 intensity is for practical purposes unaffected by the acetylene addition. This is considered as evidence for the absence of the charge exchange reaction of $C_2H_2^+$ with ethylene. Actually, at the 10:1 ratio of C_2H_2 to C_2H_4 used in the experiments, most of the $C_2H_2^+$ ions react with acetylene and never get a chance to charge exchange with ethylene. Information about charge exchange should be obtainable from this experiment, but it will be information about the charge exchange with ethylene of primarily the product ions from $C_2H_2^+$–C_2H_2 reactions. The Rudolph and Melton data on the $C_2H_2^+$–C_6H_6 charge exchange process appear to indicate that most of the ionization of the benzene observed results from interaction with secondary ions from acetylene. We believe that even in the Rudolph–Melton experiment charge exchange between $C_2H_2^+$ and C_2H_4 would be manifested by rather small changes in intensities (perhaps of the same order of magnitude as those observed in our work), and these small changes might be obscured by the major perturbation of the system resulting from flooding with a tenfold excess of acetylene.

Determination of Reaction Identities.—We now consider the determination of the identity of the ion-molecule reactions in ethylene producing the observed product ions. The reactions producing the secondary ions have been determined previously[1,7] and the most important reactions will just be summarized here. These are

$$C_2H_4^+ + C_2H_4 \longrightarrow [C_4H_8^+] \begin{cases} \longrightarrow C_4H_7^+ + H & (13a) \\ \longrightarrow C_3H_5^+ + CH_3 & (13b) \end{cases}$$

$$C_2H_3^+ + C_2H_4 \longrightarrow [C_4H_7^+] \longrightarrow C_2H_5^+ + C_2H_2 \qquad (14)$$

$$C_2H_2^+ + C_2H_4 \longrightarrow [C_4H_6^+] \begin{cases} \longrightarrow C_4H_5^+ + H & (15a) \\ \longrightarrow C_3H_3^+ + CH_3 & (15b) \end{cases}$$

Recently, Melton and Rudolph[2] have reported a mass spectrometric study of the alpha-particle radiolysis of ethylene, and from it they infer reactions for the formation of $C_4H_7^+$ and $C_4H_5^+$ which are at variance with eq. 13a and 15a, namely,

$$C_2H_4^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_3 \qquad (16a)$$

$$C_3H_5^+ + C_2H_4 \longrightarrow C_4H_7^+ + CH_2 \qquad (16b)$$

and

$$C_2H_2^+ + C_2H_4 \longrightarrow C_3H_3^+ + CH_3 \qquad (17a)$$

$$C_3H_3^+ + C_2H_4 \longrightarrow C_4H_5^+ + CH_2 \qquad (17b)$$

Several objections can be raised against reactions 16 and 17. Perhaps the most important comes from the data of Melton and Rudolph themselves. On the basis of eq. 16b, the ratio of the intensity of $C_4H_7^+$ to $C_3H_5^+$ should be a linear function of the source pressure of ethylene. From Table I of the paper of Melton and Rudolph, we have calculated values of this ratio at the ethylene source pressures of 0.05, 0.06, . . . 0.10 mm. The values are 0.11, 0.11, 0.13, 0.12, 0.13, 0.12. This constancy constitutes excellent confirmation of reaction 13a. Similarly, the ratios for the $C_4H_5^+$ and $C_3H_3^+$ currents are 0.60, 0.61, 0.91, 0.91, 0.92, 0.83. The intensities at the lower pressures are quite small and, consequently, the data scatter is greater, but there is no consistent trend in the data, and they support reaction 15a. Secondly, reactions 16b and 17b postulated by Melton and Rudolph are strongly endothermic, which not only very much decreases the likelihood that they occur but also runs counter to the experimental facts[1] that the appearance potentials of the $C_4H_7^+$ and $C_3H_5^+$ are equal to within experimental error, as are the appearance potentials of $C_4H_5^+$ and $C_3H_3^+$. Finally, if reactions 16b and 17b are indeed the paths by which $C_4H_7^+$ and $C_4H_5^+$ are formed, they are tertiary ions, and their absolute intensities should vary with the third power of the ethylene pressure or their relative intensities with second power. In Fig. 2, we plot our values of the relative intensity of the $C_4H_7^+$ (mass 55) ion as a function of the source pressure of ethylene. The plot of the relative intensity of the mass 53 ion is similar. The linearity observed shows without question that the ions cannot be formed by reactions 16 and 17, but it is quite compatible with reactions 13a and 15a. Thus, we feel justified in rejecting the reactions 16 and 17 postulated by Melton and Rudolph.

In the earlier work,[1] the reactions producing the secondary ions were deduced by means of appearance potential measurements. An attempt was made in this work to use this method on tertiary ions, but with no success whatsoever.

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(6) P. S. Rudolph and C. E. Melton, *J. Chem. Phys.*, **32**, 586 (1960).

(7) D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

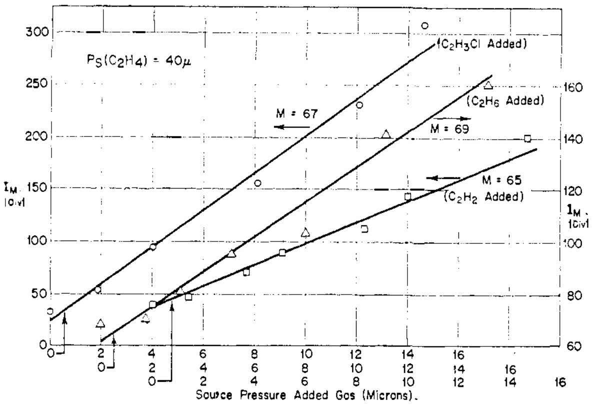

Fig. 3.—Effect of added gases on tertiary ion intensities.

Erroneously high appearance potentials were obtained for all ions, and this, plus certain other qualitative observations, led us to the conclusion that at pressures high enough to produce abundant amounts of tertiary ions sufficient electrons were removed by collision from the electron beam to form an appreciable space charge, which in turn considerably modifies the potential relationships in the ion source.

As a result, we were forced to use the mixture method[1,2] wherein the intensity of a possible reactant ion is enhanced by addition to the ethylene of a substance known to produce the ion desired in large amounts.

The experimental technique was identical with that used to investigate the charge exchange between $C_2H_2^+$ and ethylene. Ethylene in amounts sufficient to give a source pressure of 40 μ was placed in one gas handling reservoir, and varying amounts of the added gas were placed in the second reservoir. Ethane was used as the added source of $C_2H_4^+$ ion (if I_t = total ionization, $I_{28}/I_t = 0.45$, $I_{27}/I_t = 0.15$, $I_{26}/I_t = 0.10$), vinyl chloride as the source of $C_2H_3^+$ ion ($I_{27}/I_t = 0.31$, $I_{62}/I_t = 0.36$, $I_{64}/I_t = 0.11$, $I_{26}/I_t = 0.08$), and acetylene as the source of $C_2H_2^+$ ion ($I_{26}/I_t = 0.75$, $I_{25}/I_t = 0.15$). Obviously, conclusions concerning reactions occurring obtained by the mixture method will be somewhat uncertain because of the variegated nature of the ions produced by the added gas. The amount of the second gas which was added was kept as small as was feasible to keep small the occurrence of reactions which are second order in the added gas. The magnitude of the increase of the tertiary ion intensities was taken as a measure of the chemical interaction between ethylene and ions from the added gas. The occurrence of trivial mixing effects was investigated by adding argon to the ethylene. The intensities of the tertiary ions were independent of argon pressure, indicating that mixing effects were absent.

Examples of such chemical interactions are illustrated in Fig. 3 which shows the increases in the intensities of the ions of mass 65 with added acetylene, 67 with added vinyl chloride and 69 with added ethane. Similar plots were made for the ions of masses 65, 67, 69, 77 and 79 for all three of the added gases. As will be shown later, for mixtures such as we are here concerned with, we may write as a satisfactory approximation that

$$I_M = k_{MC}''\,(C_2H_4)^2(C)\tau_{C^+} \qquad (18)$$

where C is the component added to the ethylene. The ion source residence time of the ion, τ_{C^+}, is a constant for a given added component, and since the ethylene pressure is maintained constant we may write

$$I_M = k_{MC}'(C) \qquad (19)$$

The slope of I_M *vs.* (C) is $k_{MC'}$, and this may be taken as a measure of the amount of reaction between ions from C and ethylene to produce ions of mass M. We give in Table II the $k_{MC'}$ values calculated from plots such as those of Fig. 3.

It is clear from Table II that no unique choice of reactant ions can be made, if, indeed, such a choice exists. However, if as a sort of zero order approximation we assume that the largest values of $k_{MC'}$ are produced by $C_2H_4^+$, $C_2H_3^+$ and $C_2H_2^+$ as reactant ions in mixtures with ethane, vinyl chloride and acetylene, respectively, we may draw conclusions from Table II about the predominant reactant ions which give the several product ions. The reactant ions, possible reactions by which the products are formed, and the corresponding heats of reaction are given as Table Entries I–IV in Table III. The reactions are reasonable, and the heats of reaction are negative, as they must be.

TABLE II

$k_{MC'}$ VALUES. CHART DIVISIONS/MICRON, $Ps(C_2H_4) = 40\ \mu$

	M				
C	65	67	69	77	79
C_2H_6	1.5	2.6	6.7	0.15	0.51
C_2H_3Cl	[a]	17.3	1.9	16.1	0.73
C_2H_2	11.1	3.3	1.7	23.1	6.1

[a] C_2H_3Cl alone produces ions at mass 65 at high pressure.

TABLE III

TERTIARY REACTIONS (PARTIAL LIST) IN C_2H_4

Table entry	Product Ion mass	Product Ion formula	Reactant ion	Possible reaction $M^+ + 2C_2H_4 \rightarrow$	ΔH (kcal./mole)
1	65	$C_5H_5^+$	$C_2H_2^+$	$C_5H_5^+ + CH_3 + H_2$	-85^a
2	67	$C_5H_7^+$	$C_2H_3^+$	$C_5H_7^+ + CH_4$	-97^a
3	69	$C_5H_9^+$	$C_2H_4^+$	$C_5H_9^+ + CH_3$	-43^a
4	79	$C_6H_7^+$	$C_2H_2^+$	$C_6H_7^+ + H + H_2$	-55^b
5	77	$C_6H_5^+$	$C_2H_3^{+c}$	$(C_6H_5^+ + 3H_2)^c$	$-\ 4^a$
6	56	$C_4H_8^+$	$C_2H_4^+$	$C_4H_8^+ + C_2H_4$	-57^a

[a] Calculated from ΔH_f values given in Field and Franklin.[8] [b] Calculated using $\Delta H_f(C_6H_7^+) = 235$ kcal./mole.[9] [c] Uncertainties exist.

The situation concerning the mass 77 ($C_6H_5^+$) ion is clouded. The most straightforward interpretation of the data of Table II is that both $C_2H_2^+$ and $C_2H_3^+$ are strongly involved in the formation of the mass 77 ion. However, while this is energetically feasible (using ground state energetics) for vinyl ion, *viz.*

$$C_2H_3^+ + 2C_2H_4 \longrightarrow C_6H_5^+ + 3H_2 \qquad \Delta H = -4 \text{ kcal./mole} \qquad (20)$$

it is not for acetylene ion

$$C_2H_2^+ + 2C_2H_4 \longrightarrow C_6H_5^+ + 2H_2 + H \qquad \Delta H = +11 \text{ kcal./mole} \qquad (21)$$

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

(9) J. L. Franklin, F. W. Lampe and H. E. Lumpkin, *J. Am. Chem. Soc.*, **81**, 3152 (1959).

Thus a problem exists in explaining the large increase in the mass 77 intensity when acetylene is added.

First, it might be mentioned that acetylene alone forms a small amount of mass 77 tertiary ions, and consequently the amount of acetylene added in the C_2H_2–C_2H_4 mixture experiments was kept quite low (acetylene source pressure of less than 10 μ). We believe that no appreciable amount of reactions second order in acetylene is occurring in the mixture experiments.

One might postulate that C_2H^+ is the reactant, thus

$$C_2H^+ + 2C_2H_4 \longrightarrow C_6H_6^+ + 2H_2 \qquad \Delta H = -138 \text{ kcal./mole} \qquad (22)$$

The ratio of the k_{77}' values for acetylene and vinyl chloride is 1.4, and the ratio of the mass 25 intensities from these compounds is 1.9. This agreement supports the postulate, but on this basis the relative intensity of the mass 25 ion in ethane would lead one to expect a k_{77}' value for ethane which is about 10 times larger than is actually observed. An explanation which accounts for the facts is that the reaction producing the mass 77 ion in the C_2H_2–C_2H_4 mixture involves an excited $C_2H_2^+$ ion (which is not produced by fragmentation in ethane), but the mass 77 ion in pure ethylene and in C_2H_3Cl–C_2H_4 mixtures is produced from vinyl ion. This is speculation which at the present time cannot be investigated further experimentally. In this work we shall assume that vinyl ion produces the mass 77 ion in pure ethylene (reaction 20), and this reaction is entered as Table Entry 5 in Table III, but uncertainties exist.

At ethylene pressures high enough for tertiary processes to be commencing, one finds ions formed at masses 54 and 56 in amount in excess of the ^{13}C contributions from the ions at masses 53 and 55, respectively. It will be shown later that these excess ions (hereafter, in this paper, all references to ions at masses 54 or 56 should be taken to mean $C_4H_6^+$ or $C_4H_8^+$, *i.e.*, contributions of ^{13}C isotope ions will have been removed) are tertiary ions, and it is reasonable to think that they are the $C_4H_6^+$ and $C_4H_8^+$ ions previously postulated[1] as unobserved intermediates in the formation of ethylene secondary ions but here stabilized by third-body processes at the relatively high pressures.

We have attempted to investigate the identities of the reactions producing these ions by mixture studies with C_2H_2, C_2H_6 and C_2H_3Cl. The technique was identical with that used in the investigation of the C_5 and C_6 tertiary ions. The ions at masses 53, 54, 55 and 56 were measured, and plots of the intensities of these ions against the ion sources pressure of the added gas were nicely linear. The results were calculated in terms of k_{MC}' values. At mass 56, the k_{MC}' value is highest for C_2H_6, and we conclude that the mass 56 ion ($C_4H_8^+$) is formed predominantly from $C_2H_4^+$. The reactant, reaction and energetics calculated on the basis that $C_4H_8^+$ is 2-butene are given in Table III as Table entry 6. For the mass 54 ion the evidence is insufficient for the choice of a predominant reactant ion. However, some results in the early part of this work seemed to indicate that $C_4H_6^+$ is formed from $C_2H_2^+$, and in the pressure studies to be considered shortly the initial intensities of $C_2H_2^+$ ion (I_{26}^0) are calculated assuming this to be the case (eq. 7). We believe that any error involved will be trivially small.

Deductions obtained in this section concerning the reactant ions and, in particular, the actual chemical reactions, must be considered to apply only at the pressures at which the experiments were made, namely, the lowest pressures at which tertiary ions were formed in sufficient abundances for measurements to be made. As will be shown later, for some ions new processes set in at higher pressures.

No attempt has been made to determine the reactions forming the product ions with mass above 79. The experimental difficulties attendant upon making such measurements doubtless will be formidable.

Pressure Studies and Rate Constant Determinations, Masses 54–79.—Studies of the variation of the intensities of the ions in ethylene as a function of ion source pressure have been made, and from these studies deductions concerning the modes and rates of formation of the ions may be drawn.

A mathematical analysis of the kinetics of ion-molecule reactions in a mass spectrometer ionization chamber was given quite some time ago for the case of secondary ions. More recently the treatment has been generalized to include tertiary ions,[10] and since the pressure studies of the present work must be analyzed in terms of this treatment, a summary of it will be given here.

It is assumed that the reaction scheme which represents the chemical processes occurring is

$$P_i^+ + M \xrightarrow{k_{1i}} P_i M^+ \qquad (23)$$

$$P_i M^+ \xrightarrow{k_{2ij}} S_{ij}^+ + N_{ij} \qquad (24)$$

$$P_i M^+ + M \xrightarrow{k_{3i}} P_i M_2^+ \qquad (25)$$

$$P_i M_2^+ \xrightarrow{k_{4il}} T_{il}^+ + N_{il} \qquad (26)$$

$$S_{ij}^+ + M \xrightarrow{k_{5ij}} S_{ij} M^+ \qquad (27)$$

$$S_{ij} M^+ \xrightarrow{k_{6ijm}} T_{ijm}^+ + N_{ijm} \qquad (28)$$

Here M, P^+, S^+ and T^+ are, respectively, the concentrations of neutral molecules and primary, secondary and tertiary ions. PM^+, PM_2^+ and SM^+ are intermediate ions (or activated complexes) which are in low abundance and may not be observed but must necessarily be present. In this scheme tertiary ions can be formed by two different paths, namely, (1) by the decomposition of the tertiary intermediate complex $P_iM_2^+$ formed directly from the secondary intermediate complex P_iM^+ (reactions 23, 25 and 26), or (2) by the decomposition of the tertiary intermediate complex $S_{ij}M^+$ formed from the secondary product ion S_{ij}^+ (reactions 26, 29 and 30).

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[10] F. W. Lampe, J. L. Franklin and F. H. Field, "Kinetics of Reactions of Ions with Molecules," in "Progress in Reaction Kinetics," edited by G. Porter, Pergamon Press, London, to be published. The mathematical analysis is primarily due to Dr. F. W. Lampe.

If we consider the reactions involved in ethylene, the first path ($P_iM_2^+$ decomposition) is unequivocally indicated for the tertiary ions formed from $C_2H_3^+$ ($C_5H_7^+$ and $C_6H_5^+$, see Table III), since only one secondary product ion is known to be produced from $C_2H_3^+$, namely, $C_2H_5^+$; and obviously $C_5H_7^+$ and $C_6H_5^+$ cannot be formed from the reaction of $C_2H_5^+$ with one C_2H_4 molecule. The first path is also rather strongly indicated for the tertiary ions from $C_2H_4^+$ ($C_4H_8^+$ and $C_5H_9^+$). The secondary ions from $C_2H_4^+$ are $C_3H_5^+$ and $C_4H_7^+$, and the reactions of both of these with C_2H_4 to give $C_4H_8^+$ are strongly endothermic, which eliminates the reactions as possibilities. Similarly $C_4H_7^+$ can be eliminated as a precursor for $C_5H_9^+$ on the basis of endothermicity. If $C_5H_9^+$ is formed from $C_3H_5^+ + C_2H_4$, it involves simple association of the reacting partners. Such simple association has never been observed in this molecular weight range (degree of complexity), and consequently we believe that there is but a small probability that $C_3H_5^+$ is the precursor of $C_5H_9^+$. The first path is also indicated for the $C_6H_7^+$ ion from $C_2H_2^+$. The secondary ions from $C_2H_2^+ + C_2H_4$ are $C_3H_3^+$ and $C_3H_5^+$, and in the formation of $C_6H_7^+$ the first of these is contraindicated on the basis of stoichiometry and the second on the basis of endothermicity. No choice can be made for the $C_5H_5^+$ from $C_2H_2^+$, but we will assume the occurrence of the first path.

From the mathematical analysis (steady state approximation) of the kinetics of reactions 23–26, *i.e.*, assuming k_{5ij} to be negligibly small, we obtain the following relations. For secondary ions

$$\frac{I_{S_{ij}}}{I_i^0} = \frac{k_{2ij}\,(1 - e^{-k_{1i}(M)\tau})}{k_{3i}\,(M) + \sum\limits_j k_{2ij}} \qquad (29)$$

where

τ = residence time of primary ion = $\left(\frac{2dM}{eE}\right)^{1/2}$

$\tau_{28} = 9.61 \times 10^{-7}$ sec., $\tau_{27} = 9.42 \times 10^{-7}$ sec., $\tau_{26} = 9.26 \times 10^{-7}$ sec.

$I_{S_{ij}}$ = ion current corresponding to S_{ij}

I_i^0 = initial current of i'th primary ion, calculated from eq. 5–7.

At low pressures the exponential may be expanded and $k_{3i}(M)$ neglected in comparison with $\sum\limits_j k_{2ij}$, with the result

$$\frac{I_{S_{ij}}}{I_i^0} = \frac{k_{2ij}k_{1i}(M)\tau}{\sum\limits_j k_{2ij}} \qquad (30)$$

which is the expression given in ref. 1. For tertiary ions

$$\frac{I_{T_{il}}}{I_i^0} = \frac{k_{4il}k_{3i}(M)\ (1 - e^{-k_{1i}(M)\tau})}{\Sigma k_{4il}(k_{3i}(M) + \sum\limits_j k_{2ij})} \qquad (31)$$

At low pressures the exponential may be expanded and $k_{3i}(M)$ neglected in comparison with $\sum\limits_i k_{2ij}$, with the results

$$\frac{I_{T_{il}}}{I_i^0} = \frac{k_{4il}k_{3i}k_{1i}(M)^2\tau}{\sum\limits_l k_{4il} \sum\limits_j k_{2ij}} \qquad (32)$$

that is, the ratio of the tertiary ion intensity to initial primary ion intensity should be a linear function of the square of the ionization chamber pressure.

All pressure studies were made with the ion repellers at 5 v., which produces a repeller field in the ionization chamber of 12.5 volts/cm. Two series of measurements were made. Ions with masses between 26 and 79 were studied in one series made in the ionization chamber pressure range 0–360 μ and at an electron current of 0.1 μamp. Ions with masses between 65 and 105 were studied in a second series made in the ionization chamber pressure range 25–360 μ and at an electron current of 2.0 μamp. The ions of mass 65, 67, 69, 77 and 79 are common to both series and serve as tie points.

For ions in the first series (mass 26–79) the ratios $I_{S_{ij}}/I_i^0$ and $I_{T_{il}}/I_i^0$ were calculated and plotted against P_s for secondary ions and P_s^2 for tertiary ions. In all cases save one (discussed later) the initial portions of the plots were linear, and rate constants were calculated from the slopes of the linear portions using eq. 30 for secondary ions and eq. 32 for tertiary ions. The rate constants thus obtained are given in Table IV. The rate constants for the intermediate complexes P_iM^+ and $P_iM_2^+$ are calculated from the values given in Table IV by summing the rate constants for the several product ions coming from a given intermediate complex. These values are given in Table V.

TABLE IV

RATE CONSTANTS AT E = 12.5 V./CM.

Secondary ions

Product ion Mass (j)	Product ion Formula	Reactant ion Mass (i)	Reactant ion formula	Rate constant $\frac{k_{2ij}}{\sum\limits_j k_{2ij}} k_{1i} \times 10^{10}$ (cc./molecule sec.)
29	$C_2H_5^+$	27	$C_2H_3^+$	3.6
39	$C_3H_3^+$	26	$C_2H_2^+$	2.3
41	$C_3H_5^+$	28	$C_2H_4^+$	2.6
53	$C_4H_5^+$	26	$C_2H_2^+$	1.4
55	$C_4H_7^+$	28	$C_2H_4^+$	0.21

Tertiary ions

Product ion Mass (l)	Product ion Formula	Reactant ion Mass (i)	Reactant ion Formula	$\frac{k_{4il}}{\sum\limits_l k_{4il}} \frac{k_{3i}k_{1i}}{\sum\limits_j k_{2ij}} \times 10^{27}$ $\left(\frac{\text{cc.}^2}{\text{molecule}^2\ \text{sec.}}\right)$
54	$C_4H_6^+$	26(?)	$C_2H_2^+$(?)	7.6
56	$C_4H_8^+$	28	$C_2H_4^+$	2.0
65	$C_5H_5^+$	26	$C_2H_2^+$	4.3
67	$C_5H_7^+$	27	$C_2H_3^+$	1.7
77	$C_6H_5^+$	27	$C_2H_3^+$	1.5
79	$C_6H_7^+$	26	$C_2H_2^+$	1.7

The rate constants for the secondary ions produced by $C_2H_2^+$ and $C_2H_3^+$ are in excellent agreement with those obtained previously,[1] but the values for the secondary ions produced from $C_2H_4^+$ ($C_3H_5^+$ and $C_4H_7^+$) are here only about 60% of the earlier values. This discrepancy is not large enough to be concerned about.

The fact that the rate constants for ion–molecule reactions are very large is by now quite well-known. Tables IV and V show that the fast rates, heretofore observed only for second order processes, also occur with third-order processes. As a basis for comparison, it might be mentioned that Rabinowitch[11] has found rate constants for

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(11) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).

TABLE V

RATE CONSTANTS AT $E = 12.5$ V./CM.

Secondary intermediate complex ions P_iM^+

Product ion Formula	Reactant ion Mass (i)	Reactant ion Formula	Rate constant $k_{1i} \times 10^{10}$ (cc./molecule sec.)
$[C_4H_6^+]$	26	$C_2H_2^+$	3.7
$[C_4H_7^+]$	27	$C_2H_3^+$	3.6
$[C_4H_8^+]$	28	$C_2H_4^+$	2.8

Tertiary intermediate complex ions $(P_iM_2^+)$

Product ion Formula	Reactant ion Mass (i)	Reactant ion Formula	Rate constant $\frac{k_{3i}k_{1i}}{\sum_j k_{2ij}} \times 10^{27}$ $\left(\frac{\text{cc.}^2}{\text{molecule}^2\text{ sec.}}\right)$
$[C_6H_{10}^+]$	26	$C_2H_2^+$	13.5
$[C_6H_{11}^+]$	27	$C_2H_3^+$	3.1
$[C_6H_{12}^+]$	28	$C_2H_4^+$	2.0

the three-body recombination of Br atoms and I atoms ranging from about 1×10^{-32} to 100×10^{-32} cc.^{2}/molecule^2 sec. depending upon the identity of the third body. More recently, a value of 1.6×10^{-32} cc.^{2}/molecule^2 sec. has been obtained[12] for the recombination of N atoms in N_2.

In Table IV it should be noted that the rate constant for the formation of the tertiary ion at mass 54 ($C_4H_6^+$) is appreciably larger than the other tertiary rate constants, and this in turn results in a large value for $[C_6H_{10}^+]$ in Table V. It will be recalled that difficulty was encountered in identifying the nature of the reactions producing the $C_4H_6^+$ ion, consequently these rate constants (and others to be calculated from them) must be looked upon with some skepticism.

The third order rate constants given in Table V and calculated from eq. 32 are compounded of two second order constants and a first order constant, $k_{1i}k_{3i}/\Sigma k_{2ij}$. It also may be seen from Table V that the amount of variation in the second order rate constants, k_{1i}, is quite small. The second order reaction cross sections for many condensation type reactions have been tabulated,[13] and for the most part the variations are within an order of magnitude. Thus we will assume that k_{1i} and k_{3i} are equal. Then taking values of k_{1i} and $k_{1i}k_{3i}/\Sigma k_{2ij}$ from Table V, we calculate values of $\sum_j k_{2ij}$, which are given in Table VI. These are the rate constants for the various decompositions of the complexes P_iM^+, and while they are approximate, they may well be the first completely experimentally determined rate constants for the unimolecular decomposition of ions.

TABLE VI

TOTAL UNIMOLECULAR DECOMPOSITION RATE CONSTANTS, $\sum_j k_{2ij}$

Ion, P_iM^+	Mass	$\sum_j k_{2ij} \times 10^{-7}$
$C_4H_6^+$	54	1.0
$C_4H_7^+$	55	4.3
$C_4H_8^+$	56	4.0

It is now of considerable interest to calculate I_{Sij}/I_i^0 from eq. 31 and I_{Til}/I_i^0 from eq. 33 using the rate constants tabulated in Tables V and VI and compare the values thus calculated with experimental values. It will be noted that eq. 31 contains the term $k_{4il}/\Sigma k_{4il}$, which determines the fraction of the tertiary complexes $P_iM_2^+$ that dissociate in such a manner as to form the tertiary ion T_l. This term can be calculated accurately if a complete knowledge of the dissociation modes of $P_iM_2^+$ is available. Actually, we believe that our knowledge of these modes is more or less incomplete, and consequently we shall feel that in using eq. 31 the value of $k_{4il}/\Sigma k_{4il}$ may be adjusted arbitrarily a little without provoking a justified charge of blatant empiricism.

It is convenient to discuss the various product ions individually.

Mass 29, $C_2H_5^+$.—The experimental points and the line calculated from eq. 31 are given in Fig. 4. Mass 27 produces only mass 29 as a secondary product ion and, consequently, $k_{2,27,29} = \sum_j k_{2,27j} = 4.3 \times 10^7$ sec.$^{-1}$ from Table VI.

Mass 39, $C_3H_3^+$.—The experimental points and the line calculated from eq. 29 are given in Fig. 5. Mass 26 produces secondary product ions at mass 39 and 53, and $k_{2,26,39}$ may be calculated from Table V and Table VI[14] to be 0.62×10^7 sec.$^{-1}$.

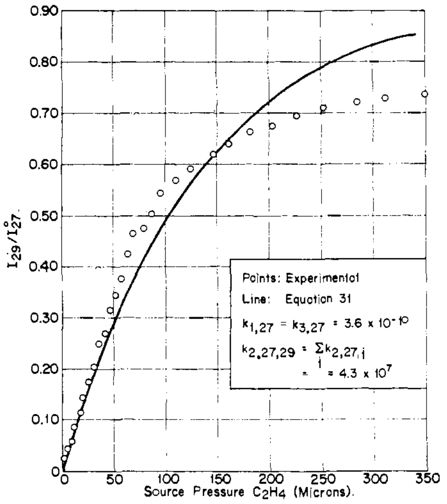

Fig. 4.—Mass 29 ($C_2H_5^+$) calculated and experimental pressure plots.

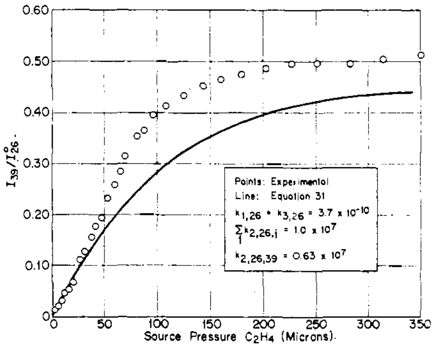

Fig. 5.—Mass 39 ($C_3H_3^+$) calculated and experimental pressure plot.

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(12) J. T. Herron, J. L. Franklin, P. Bradt and V. H. Dibeler, *J. Chem. Phys.*, **30**, 879 (1959).

(13) F. W. Lampe and F. H. Field, *Tetrahedron*, **7**, 189 (1959).

(14) $[2.3 \times 10^{-10}/(2.3 \times 10^{-10} + 1.4 \times 10^{-10})]\,(1.0 \times 10^7) = 0.62 \times 10^7$.

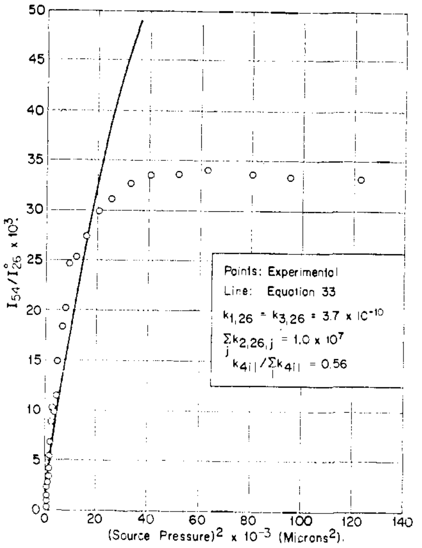

Fig. 6.—Mass 54 ($C_4H_6^+$) calculated and experimental pressure plots.

Mass 41, $C_3H_5^+$.—The experimental points and the line calculated from eq. 29 are of about the same form as was found for mass 39 (Fig. 5). The value of $k_{2,28,41}$ is calculated from Tables IV and VI to be 3.7 × 10^7 sec.$^{-1}$. Ethylene forms two other secondary ions of significant intensity, namely, those of masses 53 and 55. The pressure plots of these are also similar in form to that of the mass 39 ion.

The agreement between the experimental points and the calculated lines for the mass 29, 39 and 41 ions is good. Unfortunately, the form of eq. 29 is such that identical relative changes in the magnitudes of k_{3i}, Σk_{2ij} and k_{2ij} have only trivial effects upon the calculated ion current ratios. Thus the calculated curves give no information about the correctness of the absolute magnitudes of the constants. However, from some trial and error calculations we are of the opinion that the agreement observed between the experimental and calculated current ratios signifies that the relative values of k_{3i} and Σk_{2ij} are correct to within a factor of 10. That is, for example, if for mass 41, the value of k_{3i} is 2.8 × 10^{-10}, the value of Σk_{2ij} is not smaller than about 4 × 10^6.

Mass 54, $C_4H_6^+$.—The experimental points and the line calculated from Eq. 31 are given in Fig. 6. The value of $k_{4il}/\sum_l k_{4il}$ is calculated from Table IV. Obviously the experimental variation of the current ratio is not at all represented by the calculated line. The same kind of calculated and experimental plots (and therefore the same kind of divergence between the two) is found for the product ions at mass 65 ($C_5H_5^+$) and 77 ($C_6H_5^+$).

Mass 67, $C_5H_7^+$.—The experimental points and the line calculated from eq. 31 are given in Fig. 7. The value of $k_{4il}/\Sigma k_{4il}$ which one calculates from Table IV is 0.53, and the use of this in eq. 31 gives current ratios which are slightly lower than the experimental values. However, the form of the calculated curve seemed to be about the same as that of the experimental curve, and as a result the value of $k_{4il}/\Sigma k_{4il}$ was arbitrarily changed to 0.75. The beautiful agreement between calculated and experimental curves shown in Fig. 7 resulted. Experimental curves of the same form are found for the product ions at mass 56 ($C_4H_8^+$) and 79 ($C_6H_7^+$), and the agreement between the experimental and calculated curves is almost as good as that for the mass 67 ion. In the case of the mass 56 ion the value of $k_{4il}/\sum_l k_{4il}$ as calculated from Table IV is 1.0, and in the case of the mass 79 ion it is 0.12. However, this was arbitrarily adjusted to 0.18.

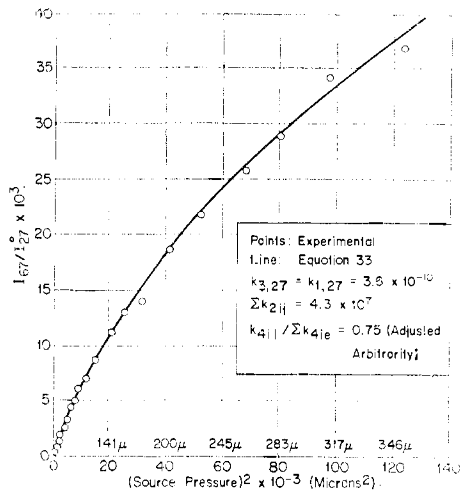

Fig. 7.—Mass 67($C_5H_7^+$) calculated and experimental pressure plots.

The form of eq. 31 is such that identical relative changes in the values of k_{3i} and Σk_{2ij} do not change the magnitude of the calculated ion current ratios much, and the agreement between the calculated and experimental pressure plots does not necessarily mean that the values used for these quantities are correct. However, the current ratios are very sensitive to the relative values used for the rate constants, and from some trial and error calculations we are of the opinion that the agreement between the calculated and experimental pressure plots for the mass 56, 67 and 79 ions means that the relative values of the rate constants for these ions are correct to well within a factor of 10.

We cannot explain the major discrepancy between the calculated and experimental current ratios for the mass 54, 65 and 77 ions. The only way in which Eq. 31 could be forced to reproduce the very sharp bend in the pressure plots at 20–30 × 10^3 μ^2 is by the use of quite unrealistic rate constants, and it is better to admit that the kinetic scheme on which Eq. 31 is based probably is not valid for these ions. One way in which the scheme obviously is inadequate is that it does not take into account subsequent reactions which must occur to produce the observed ions with masses above 84. However, the intensities of the high mass ions may be too low for this explanation to be valid. It should be noted that tertiary ions with current ratios which both agree and disagree with Eq. 31 are formed from both mass 26 and 27 reactant ions. As a consequence, we are some-

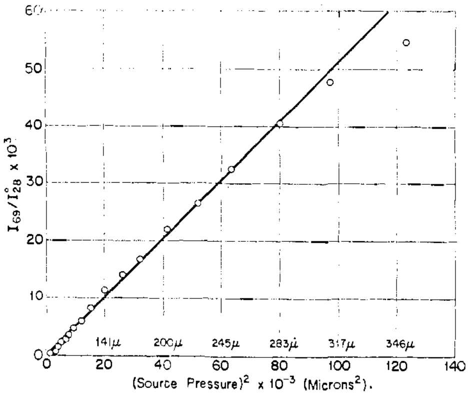

Fig. 8.—Mass 69 ($C_5H_9^+$) experimental pressure plot.

what disinclined to think that the discrepancies are the result of some experimental or procedural error such as an erroneous identification of reactant ions.

The mass 69 ($C_5H_9^+$) ion must be considered as a special case. Fig. 8 contains the pressure plot (against P_s^2) of I_{69}/I_{28}^0 over the complete pressure range studied, and in Fig. 9 the lower portion of the curve is given on a larger scale. Also given in Fig. 9 is the pressure plot of I_{56}/I_{28}^0 for comparison purposes. Comparing the plot of Fig. 8 with those of Fig. 6 and 7, it is clear that the plot for mass 69 is of the form of neither the plot of Fig. 6 (masses 54, 65 and 77) nor that of Fig. 7 (masses 56, 67 and 79). In particular, the curvature away from the ordinate which sets in at about 100 μ source pressure for the mass 67 plot does not commence below a source pressure of about 300 μ for mass 69. The plot for mass 69 shown in Fig. 9 has an unmistakable upward curvature, which is to be contrasted with the excellent linearity of the mass 56 plot. The conclusion one must draw from both Figs. 8 and 9 is that the mass 69 ion intensity increases more rapidly with pressure than is to be expected or is otherwise observed with tertiary ions. We thus postulate that the mass 69 ion is produced at least partially by a fourth-order process; that is, it is partially a quaternary ion. From the fact that the mass 69 ion begins to appear at about the same pressure as the mass 54, 56, . . .79 ions we believe that the ion is formed at relatively low pressure by a third-order process, which is almost certainly

$$C_2H_4^+ + 2C_2H_4 = C_5H_9^+ + CH_3 \qquad \Delta H = -43 \text{ kcal./mole} \quad (33)$$

If we assume that this tertiary reaction predominates below pressures of about 50 μ, we calculate from Fig. 9 a value of 0.62 × 10^{-27} for $(k_{4il}/\Sigma k_{4il})(k_{3i}k_{1i}/\Sigma k_{2ij})$. At higher pressures the fourth-order process predominates. Several reasonable reactions can be written, namely

$$C_2H_4^+ + 3C_2H_4 \longrightarrow C_5H_9^+ + \begin{array}{l} C_3H_8 \\ CH_4 + C_2H_4 \\ C_2H_5 + CH_3 \end{array} \left\{ \begin{array}{lr} \Delta H = -112 \text{ kcal./mole} & (34a) \\ \Delta H = -\ 92 \text{ kcal./mole} & (34b) \\ \Delta H = -\ 32 \text{ kcal./mole} & (34c) \end{array} \right.$$

Pressure Studies, Masses 81–105.—The mass scans involved in making the pressure studies on these ions covered the mass range 60–105, and they were made in a different series and at a higher electron current (2.0 μamp.) than those for the ions discussed in the preceding section. Since we have no knowledge concerning the identity of the reactant ions for the various product ions, it is not possible to determine the order of the process resulting in a given product ion by the technique used in the preceding section, namely, from the pressure variation of the ratio of the product ion intensity to the initial intensity of the reactant ion. Instead, we shall form ratios of product ions. If a ratio remains essentially constant as a function of pressure, it will be considered that the two ions are produced by processes of the same kinetic order. On the other hand, if the ratios vary with pressure, the kinetic orders will be considered to be different. This criterion of kinetic order will be valid only in the absence of complicating factors, of which one can easily conceive quite a few.

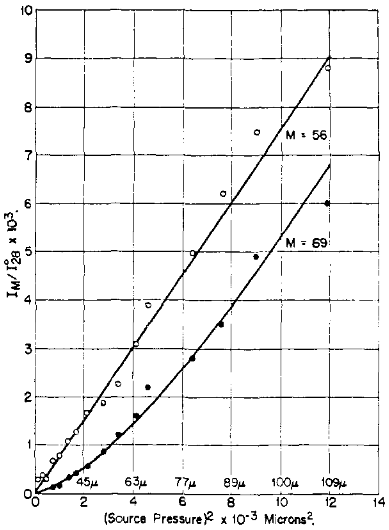

Fig. 9.—Mass 56 ($C_4H_8^+$) and 69 ($C_5H_9^+$) experimental pressure plots, expanded scale.

In an attempt to evaluate the extent to which this criterion could be trusted, intensity ratios at different pressures were calculated for some of the ions in the 26–79 mass range. Usually satisfactory behavior was observed, but occasionally misleading results were obtained. The value of I_{67}/I_{41} increased linearly in the pressure range 0–350 μ, as one would expect for the ratio of a tertiary to a secondary ion. On the other hand, the value of I_{39}/I_{41} decreased by a factor of 10 in the same pressure range, which is hardly to be expected of two secondary ions.

Fig. 10 shows the pressure variation of I_{69}/I_{67} and I_{91}/I_{69}. Mass 67 is without much question a tertiary ion, so the form of the $I_{69}/_{67}$ plot is consistent with the postulate made above that at low pressures (50–100 μ) the mass 69 ion is produced predominantly by a tertiary process, but at high pressures the process is predominantly quaternary. This interpretation is buttressed by the I_{91}/I_{69} variation. Mass 91 ($C_7H_7^+$) from stoichiometry cannot be formed from less than four ethylenes (molecules, ions or fragments), and consequently it must be formed by at least a quaternary process. The gentle decrease in the current ratio followed by an essentially constant value over the pressure

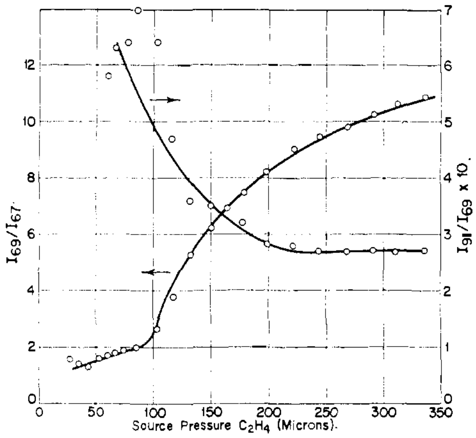

Fig. 10.—Current ratios (I_{69}/I_{67} and I_{91}/I_{69}) *vs.* source pressure.

range 150–350 μ is most easily interpreted as meaning that at high pressures both the mass 69 and 91 ions are formed by quaternary processes.

The ratio of the mass 103 ion ($C_8H_7^+$) intensity to that of the mass 91 ion remains satisfactorily constant (to within 30–40%) over the pressure range from 50–350 μ. Also the form of the plot of I_{103}/I_{69} is identical with that of I_{91}/I_{69}, and one may confidently conclude that the mass 103 ion is also formed by a quaternary process.

Fig. 11 shows the pressure variation of I_{105}/I_{103}. A linear plot is also obtained for the pressure variation of I_{105}/I_{69}, and both of these plots lead to the conclusion that the mass 105 ($C_8H_9^+$) ion is formed from ethylene by a fifth-order process. Similarly, I_{81}/I_{69} increases linearly with pressure, which indicates that the mass 81 ($C_6H_9^+$) ion is also formed by a fifth-order process. Stoichiometry does not demand that either the mass 105 or the mass 81 ions be formed by fifth-order processes. However, this work and all other studies of ion-molecule reactions in hydrocarbons illustrate the extent to which C-C bond fission occurs in forming the product ions from the intermediate complexes; thus stoichiometry determines only the minimum kinetic order by which a product ion is formed. For example, the mass 119 ion ($C_9H_{11}^+$) found in this work (see Table I) must be formed by at least a fifth-order process, and the occurrence of a fifth-order process here lends support to the postulate of fifth-order processes being involved in the formation of the mass 81 and 105 ions.

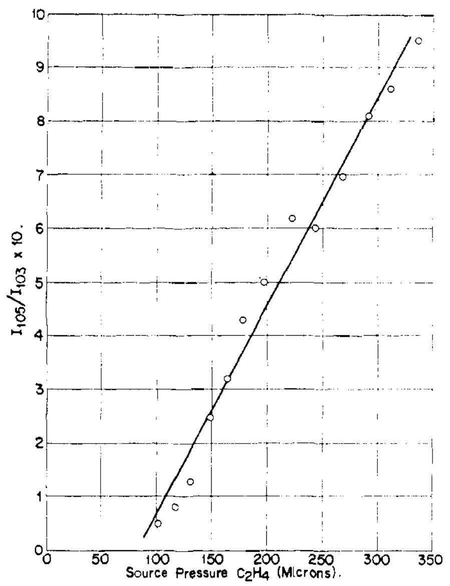

Fig. 11.—Current ratio (I_{105}/I_{103}) *vs.* source pressure.

Finally, I_{97}/I_{105} rises linearly with pressure, which indicates that the mass 97 ion ($C_7H_{13}^+$) is formed by a sixth-order process. Thus one finds in the ethylene mass spectrum at ion source pressures of 200–300 μ ions formed by processes with kinetic orders ranging from one to six. It must be mentioned that some of the ions probably are formed in certain pressure ranges simultaneously by processes of different orders. We have postulated this sort of behavior for the mass 69 ion, and we suspect it for other ions. It is completely reasonable to think that in certain pressure ranges there could occur simultaneously the reactions

$$C_2H_4^+ + C_2H_4 \longrightarrow C_3H_5^+ + CH_3 \qquad (35a)$$

$$C_2H_4^+ + 2C_2H_4 \longrightarrow C_3H_5^+ + C_3H_7. \qquad (35b)$$

Furthermore, the pressure plots of the secondary ions (Fig. 5 and 6) tend to be higher than one calculates for pressures above 50 μ, and this could be the result of the contribution of tertiary reactions such as eq. 35b.

Acknowledgments.—Most of the measurements reported in this paper were made by Mr. W. C. Gieger. I wish gratefully to acknowledge the extensive, competent and cheerful service he has rendered.