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Ion-Molecule Reactions in Acetylene

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Ion-molecule reactions occurring in acetylene have been studied up to a pressure of 0.3 torr inside the ion source of the mass spectrometer. Long-chain ionic reactions have been recognized leading to the formation of high-order ions. A full kinetic study has been carried out, and a mechanism is proposed for these reactions.

Ion-molecule reactions occurring in acetylene when bombarded by low energy electrons in the ion source of a mass spectrometer have been recognized by several investigators,¹⁻⁵ but apart from the work of Bloch,⁵ all the earlier works were confined to low pressures of acetylene, and, consequently, very few product ions had been observed. Bloch, however, has succeeded in reaching a pressure of 10^{-2} torr of acetylene inside the ion source of his spectrometer and has reported polymeric ions of up to $C_8H_8^+$ which were not detectable at lower pressure.

Using α -particles emitted from Po^{208} as the source of irradiation, Rudolph and Melton⁶ have studied ion-molecule reactions in acetylene up to a pressure of 0.1 torr, but the largest polymeric ions they were able to detect with reasonable intensity were $C_6H_6^+$ and $C_6H_4^+$. The failure to observe larger ionic species might have been due to the rather weak primary ionic current obtainable with such sources of radiation.

More recently, Lindholm, Szabo, and Wilmenius,⁷ in their study of charge-exchange processes between acetylene and some positive ions, have obtained direct evidence for the formation of secondary ionic species owing to the reaction of primary acetylene ions with acetylene molecules.

Of all the above-mentioned investigators, only Field, Franklin, and Lampe,² Barker, Hamill, and Williams,³ and Fuchs⁴ have attempted full kinetic studies of some of the secondary processes in acetylene, but, because of the rather low pressure then attained, they were only able to study the production of a few secondary ions at mass numbers 37-39 and 49-52 corresponding to C_3 and C_4 ions.

In this laboratory, with low energy electrons as the source of ionization, pressures of up to a few hundred microns have been obtained inside the ion source of the mass spectrometer. It was therefore decided to undertake the study of ion-molecule reactions occurring in acetylene in the wide pressure range of 0.008-0.3 torr, both to ascertain the extent of such reactions and to give, as far as possible, full kinetic data for the major reactions. These reactions will undoubtedly prove to be of great value for the elucidation of the mechanism of radiolysis of acetylene as has been suggested by several recent studies.^{8,9}

Experimental

Because the essential features of the apparatus have been described in a fragmentary manner in previous

(1) Hinkle, Roberts, and Hamner, paper presented at meeting of A.S.T.M. Committee E-14, Cincinnati, Ohio, May 28 to June 1, 1956 (quoted in ref. 2).

(2) F. H. Field, J. L. Franklin, and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2665 (1957).

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

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

(5) A. Bloch, *Advan. Mass Spectrometry*, **2**, 48 (1963).

(6) P. S. Rudolph and C. E. Melton, *J. Phys. Chem.*, **63**, 916 (1959).

(7) E. Lindholm, I. Szabo, and P. Wilmenius, *Arkiv Fysik*, **25**, 417 (1963).

(8) L. M. Dorfman and A. C. Wahl, *Radiation Res.*, **10**, 680 (1959).

(9) F. H. Field, *J. Phys. Chem.*, **68**, 1039 (1964).

publications,¹⁰ a brief summary will be given here for the sake of completeness.

The mass spectrometer employed is Italelectronica SP21F 15-cm. radius of curvature, Nier-Type 60°-sector analyzer instrument, modified for research purpose in the ion detector, pumping system, and operating conditions of the ion source. The ion detector consists of a 17-stage, copper-beryllium ion multiplier backed by a d.c. linear amplifier. Its maximum sensitivity, limited by background noise, can be estimated to be $\sim 5 \times 10^{-18}$ amp.

The adopted differential pumping system makes it possible to keep a very high jump of pressure between the ion source, its surroundings, and the analyzer tube, the order of pressure in these sections being, respectively, 10^{-3} – 10^{-1} , $<10^{-4}$, and $<10^{-5}$ torr. The analyzer tube and ion source section are connected together through a slit 10×0.25 mm.

The ion source is of cylindrical section (17.5-mm. diameter) and is fitted with a plane repeller electrode. The ion exit slit is 2×0.1 mm., and the defining slit of the ionizing electron beam is 0.5×0.1 mm. The average geometric distance between the electron beam and the exit slit is 0.335 cm. Under normal operating conditions a repeller field of 10 v. cm^{-1} and trap current stabilized at about $0.6 \mu\text{a}$. are used. No particular arrangements are available to limit the thermal spread in energy of the ionizing electrons which are emitted from a hot tungsten filament. The temperature of the ion source is measured by a Pt-resistance thermometer with a precision of $\pm 2^\circ$; in the present work the temperature of the source during measurements varied in the region 150 – 160° .

The concentration of the gas inside the ion source was determined indirectly by calibration using the cross sections of decay of primary ions from methane in the manner described previously.¹¹ In this work, the gas concentration used was varied over the range 2 – 60×10^{14} molecules cm^{-3} , corresponding to gas pressure of about 0.008 – 0.3 torr.

Commercially available, good quality acetylene was purchased locally. It was subjected to very careful drying and subsequently purified by several bulb-to-bulb distillations. The samples used were all analyzed mass spectrometrically and were found to be of purity better than 99.6%.

Results

I. High Pressure Mass Spectrum of Acetylene.

The mass spectrum of acetylene measured at 0.26 torr inside the ion source with an electron beam energy of 80 v. and a repeller field of 10 v. cm^{-1} is given in Table I. The highest m/e observed is at 179 corresponding to $\text{C}_{14}\text{H}_{11}^+$, but the largest contribution to the total ion current is from the C_8 ions (52%) and from the C_8 ions (28%). Another interesting point to note is that the abundance of ions with an even number of carbon atoms is much higher than that of ions with an odd number of carbon atoms; the ratio $\Sigma I_{\text{odd}}/\Sigma I_{\text{even}} = 0.05$.

(10) A. Giardini-Guidoni and G. G. Volpi, *Nuovo Cimento*, **17**, 919 (1960); A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, **26**, 845 (1962); *J. Chem. Phys.*, **39**, 518 (1963).

(11) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *ibid.*, **39**, 1599 (1963).

Table I. Mass Spectrum of Acetylene at 0.26 Torr inside the Ion Source. Electron Beam Energy 80 V.^a and Repeller Field 10 V. Cm^{-1} (Based on $\Sigma I = 100$)

m/e	Positive ion	% abundance ^b	m/e	Positive ion	% abundance ^b
12	C	0.02	77	C_6H_5	25
23	CH	0.03	78	C_6H_6	0.79
24	C_2	...	86	C_7H_2	0.1
25	C_2H	0.03	87	C_7H_3	1.1
26	C_2H_2	0.29	88	C_7H_4	1.8
27	C_2H_3	0.22	89	C_7H_5	0.48
37	C_3H	0.06	98	C_8H_2	0.08
38	C_3H_2	0.07	99	C_8H_3	...
39	C_3H_3	1.2	100	C_8H_4	2.9
48	C_4	...	101	C_8H_5	0.91
49	C_4H	...	102	C_8H_6	11
50	C_4H_2	0.6	103	C_8H_7	13
51	C_4H_3	2.4	112	C_9H_4	0.14
52	C_4H_4	1.6	113	C_9H_5	0.14
53	C_4H_5	2.9	114	C_9H_6	0.17
62	C_6H_2	0.31	115	C_9H_7	0.04
63	C_6H_3	1.9	126	C_{10}H_6	0.79
64	C_6H_4	0.01	127	C_{10}H_7	0.34
65	C_6H_5	0.46	128	C_{10}H_8	0.15
74	C_6H_2	0.33	153	C_{12}H_9	0.5
75	C_6H_3	1.4	179	$\text{C}_{14}\text{H}_{11}$	0.1
76	C_6H_4	24			

^a All electron energy values reported in this work are nominal.
^b Corrected for C^{13} .

Comparison of the high pressure mass spectrum reported in Table I with the zero-pressure-extrapolated primary mass spectrum of acetylene (C_2H_2^+ , 74; C_2H^+ , 12; C_2^+ , 4; CH^+ , 6; C^+ , 4; all figures refer to percentage abundance relative to $\Sigma I = 100$) shows the great reactivities of the primary ions.

The mass spectrum of acetylene has also been measured at 15- and 18-v. electron beam energies where, in the former, C_2H_2^+ and, in the latter, C_2H_2^+ and C_2H^+ are practically the only primary ions present. These simplified spectra show a preponderance of even carbon number ions over odd, the ratio $\Sigma I_{\text{odd}}/\Sigma I_{\text{even}}$ becoming increasingly small in the order $80 > 18 > 15$ v. Further reference shall be made to these measurements in the following section.

II. Ionization Efficiency Data. The most direct means available for ascertaining the precursor of a given product ion is the matching of their ionization efficiency curves. However, for reliability and reproducibility a relatively low pressure must be used.^{12–15} The only product ions of measurable intensity at such pressure inside the ion source are C_4H_2^+ and C_4H_3^+ at m/e 50 and 51, respectively. It was therefore decided to determine the ionization efficiency curves of these two ions, together with those of the primary ions C_2H_2^+ and C_2H^+ , to study the manner in which these curves vary with pressure, and to use the results so obtained as controls for the ionization efficiency curves of the other ions which can only be measured at much higher pressure where their signals become strong enough for such measurements. The ionization

(12) L. Friedman, F. A. Long, and M. Wolfsberg, *ibid.*, **31**, 755 (1959).

(13) F. H. Field and J. L. Franklin, *Advan. Mass Spectrometry*, **2**, 484 (1963).

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

(15) G. A. W. Derwish, A. Galli, A. Giardini-Guidoni, and G. G. Volpi, *J. Am. Chem. Soc.*, **86**, 4563 (1964).

efficiency curves for m/e 25, 26, 50, and 51 are shown in Figure 1 from which it can clearly be seen that the curves for m/e 26 and 51 are essentially very similar in all respects while the curve for m/e 50 is markedly different. In fact, when it is compared with the curve for m/e 25, one is immediately led to suppose that $C_4H_2^+$ may be formed by concurrent reactions from $C_2H_2^+$ and C_2H^+ . Of course, other explanations may be put forward for such a behavior of the ionization efficiency curve of $C_4H_2^+$, but fuller discussion of this point will be presented later.

To supplement and confirm the results obtained from ionization efficiency data, recourse is made to the fact that the appearance potentials of primary ions from acetylene are widely separated,¹⁶ and, therefore, it was found useful to measure the complete spectrum of acetylene at high pressures with the electron beam energy near the appearance potential of $C_2H_2^+$. Such measurements, carried out at 15-v. electron beam energy, where $C_2H_2^+$ was the main primary ion present, and at zero pressure, accounted for nearly 100% of the ion current. The results so obtained show that almost all the even-C-number ions are products of reactions with $C_2H_2^+$ as the primary precursor. Of course, this does not in any way exclude the fact that some of these ions may also be related at high electron beam energy to other primary ions through concurrent reactions with acetylene, as, for example, in the case of $C_4H_2^+$ discussed above. In order to throw some light on the possibility that such reactions may take place in acetylene, the usual ionization efficiency curves are invaluable. Thus, other ions which were found to have ionization efficiency curves similar to that of $C_4H_2^+$ are $C_2H_3^+$, $C_3H_3^+$, $C_6H_3^+$, $C_6H_3^+$, and $C_6H_4^+$, indicating again their possible formation through concurrent reactions involving $C_2H_2^+$ and C_2H^+ as their primary ion precursors. Confirmation of this supposition is sought in measuring the mass spectrum of acetylene at an electron beam energy of 18 v. which is just above the appearance potential of C_2H^+ . The results showed that the increase in the intensity of the ions at m/e 27, 39, 50, 75, and 76, as compared with their intensities at 15-v. electron beam energy at the same pressure of gas inside the ion source, paralleled the amount of C_2H^+ produced.

Other ions which showed such mixed parentage are indicated in Table II which gives a summary of the

Table II. Parent-Daughter Ion Relationships in Acetylene

Parent ion	Daughter ions
	$C_2H_3^+,^a$ $C_3H_3^+,^a$ $C_4H_2^+,^a$ $C_4H_3^+$, $C_4H_4^+$, $C_4H_5^+,^a$ $C_6H_3^+,^a$ $C_6H_2^+,^a$ $C_6H_3^+,^a$ $C_6H_4^+,^a$ $C_6H_5^+$, $C_6H_6^+$, $C_7H_3^+,^a$ $C_7H_4^+,^a$ $C_8H_4^+,^a$ $C_8H_5^+,^a$ $C_8H_6^+,^a$ $C_8H_7^+$, $C_{10}H_6^+$, $C_{10}H_7^+$, $C_{10}H_8^+$
C_2H^+	$C_2H_3^+$, $C_3H_3^+$, $C_4H_2^+$, $C_4H_3^+$, $C_5H_3^+,^a$ $C_6H_5^+$, $C_6H_5^+$, $C_6H_4^+$, $C_7H_3^+,^a$ $C_7H_5^+,^a$ $C_8H_5^+$, $C_8H_6^+$
C_2^+	$C_3H_2^+$, $C_3H_3^+$, C_4H^+ , $C_6H_2^+$, $C_7H_3^+,^a$ $C_7H_5^+$, $C_8H_2^+$, $C_8H_3^+$, $C_8H_4^+$
CH^+ C^+	C_3H^+ , $C_5H_2^+$, $C_7H_2^+$, $C_7H_3^+$, $C_7H_4^+$, $C_9H_4^+$, $C_9H_5^+$, $C_9H_6^+$

^a These ions are also formed from a lower primary ion.

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

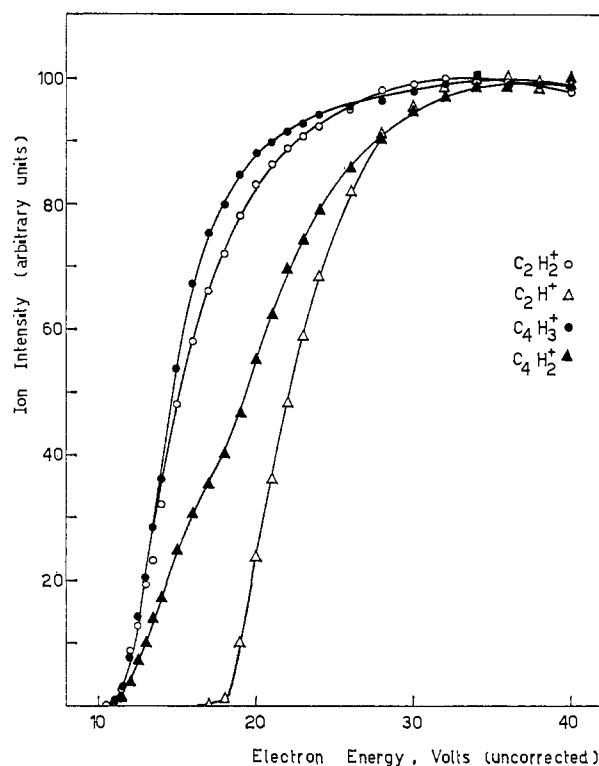


Figure 1. Ionization efficiency curves measured at a pressure of 10^{-4} torr.

results contained from ionization efficiency curves, appearance potentials, and such other measurements as indicated in the previous paragraphs.

III. Pressure Dependence of Ion Currents. (a) Primary Ions. For the study of the kinetics of ion-molecule reactions taking place inside the ion source, the variation of normalized ion intensity with pressure is investigated at 15- and 80-v. electron beam energies.

At 15- and 80-v. electron beam energies and over the wide pressure range corresponding to $2-20 \times 10^{14}$ molecules cm^{-3} , all the primary ions in acetylene were found to follow the simple exponential attenuation law $I_P = I_P^0 \exp[-\sigma^l G]$, where I_P is the normalized ion intensity (obtained by dividing the ion current by the total ion current at any given value of the pressure), and I_P^0 is its extrapolated value at zero pressure (obtained by extrapolating to zero pressure the semi-logarithmic plot of ion intensity vs. pressure curve). The total cross section of decay of the primary ion is σ^l . The pressure inside the ion source is G which is expressed in molecules cm^{-3} ; l is the distance between the electron beam and the exit slit in cm.

The dependence of the normalized intensities for the two major primary ions $C_2H_2^+$ and C_2H^+ on acetylene concentration inside the ion source is illustrated in Figure 2 from which it can be seen that the plots show marked deviation from linearity at gas concentrations greater than 20×10^{14} molecules cm^{-3} . Such behavior at high pressure has also been observed by others in the case of methane¹⁷ and ethylene.¹⁸ In these two cases,^{17,18} as well as in the present one, it is interesting to note that the deviation from the exponential decay law takes place at around 0.1 torr.

(17) F. H. Field, J. L. Franklin, and M. S. Munson, *J. Am. Chem. Soc.*, 85, 3575 (1963).

(18) S. Wexler and R. Marshall, *ibid.*, 86, 781 (1964).

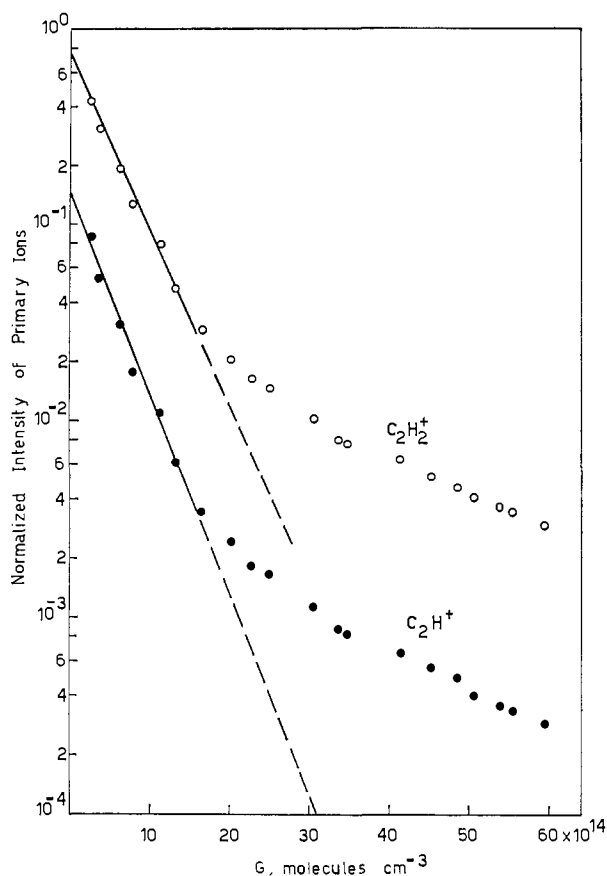


Figure 2. Semilogarithmic plots of the normalized intensity of the primary ions $C_2H_2^+$ and C_2H^+ vs. acetylene concentration (80-v. electron beam energy).

The cross sections of decay of the primary ions have been calculated from the slopes of the straight-line portions of the semilogarithmic plots of normalized ion intensities vs. acetylene concentration. The results so obtained are recorded in Table III together with those reported by others. The general agreement between the old results and the present ones is rather good considering the large difference in the experimental conditions used.

Table III. Total Cross Sections of Decay of Primary Ions in Acetylene (the Repeller Field and the Ion Path Length Are Quoted below the Authors' Names)

Primary ion	Cross section, 10^{-16} cm. ² molecule ⁻¹			
	F.F.L. ^a 10 v. cm. ⁻¹ 0.05 cm.	B.H.W. ^b 7.4 v. cm. ⁻¹ 0.135 cm.	F. ^c 13 v. cm. ⁻¹ 0.1 cm.	This work 10 v. cm. ⁻¹ 0.335 cm.
$C_2H_2^+$	77	85	97	62
C_2H^+	68
C_2^+	68	81	113	72
CH^+	58	167	205	45
C^+	45

^a See ref. 2. ^b See ref. 3. ^c See ref. 4.

(b) *Product Ions.* The complexity of the spectrum of acetylene at high pressure, as shown in Table I, makes it important to gain the fullest information possible from the pressure dependence studies to make use, from the outset, of the results given in the previous section and summarized in Table II. Thus, it is pos-

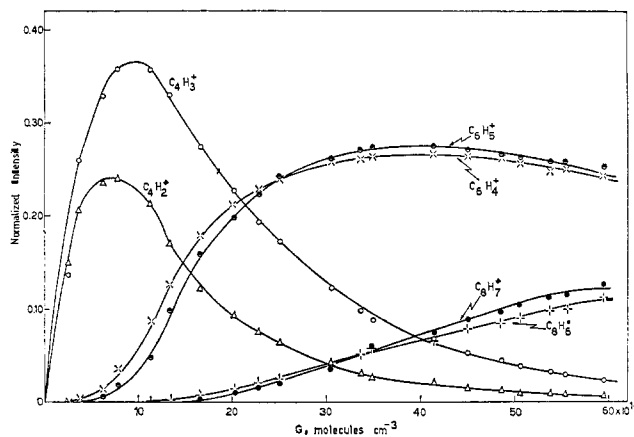


Figure 3. Normalized intensity of the major even-C-number ions vs. acetylene concentration (80-v. electron beam energy).

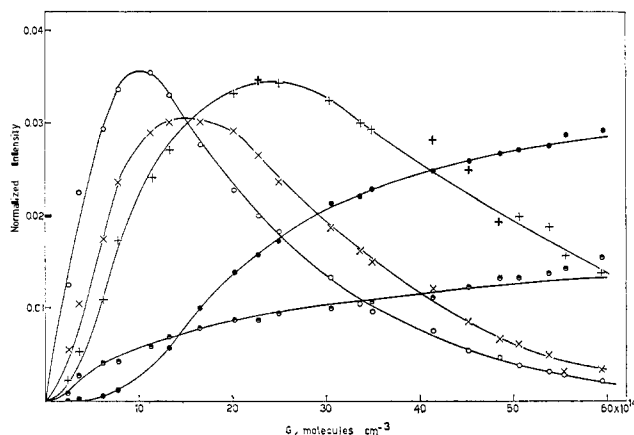


Figure 4. Normalized intensity of some even-C-number ions vs. acetylene concentration (80-v. electron beam energy): $C_2H_3^+$, \circ ; $C_4H_4^+$, \ominus ; $C_4H_5^+$, \bullet ; $C_6H_2^+$, \times ; $C_6H_3^+$, $+$.

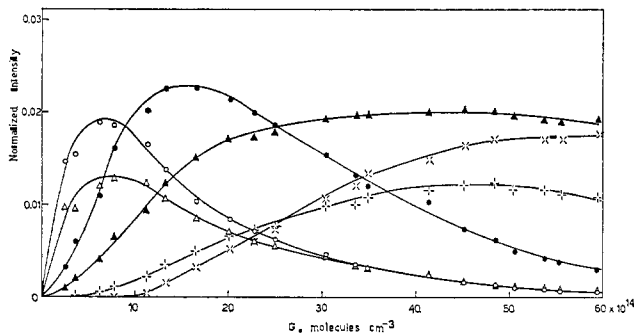


Figure 5. Normalized intensity of the major odd-C-number ions vs. acetylene concentration (80-v. electron beam energy): C_3H^+ , \circ ; $C_5H_2^+$, \triangle ; $C_5H_3^+$, \bullet ; $C_7H_3^+$, \blacktriangle ; $C_7H_4^+$, \times .

sible to divide all product ions into two main classes: (A) ions with an even number of carbon atoms (even-C-number ions) which are formed mainly from $C_2H_2^+$ as the primary ion precursor with some contribution from C_2H^+ and (B) ions with an odd number of carbon atoms (odd-C-number ions) which are formed by reaction paths involving mainly the other primary ions, viz., C_2^+ , CH^+ , and C^+ , as precursors.

The pressure dependence of the normalized intensities of the major ions belonging to the two classes is illustrated in Figures 3-5.

In order to be able to suggest mechanistic paths for the formation of the product ions in acetylene, it is important to establish the kinetic order of as many of these ions as possible. Simple theory indicates that, in the range of low pressure, the normalized intensity of a product ion of the n th order is a function of the concentration of the gas inside the source; thus $I_n = \text{constant} \times G^{n-1}$, and a plot of I_n against G raised to the correct power should initially be a straight line. From such plots and also from plots of the ratios of intensities of ions belonging to the same reaction sequence but with a difference of one in their kinetic orders, it was possible to ascertain the order of most product ions; the results are given in Table IV. However, it must be noted here that the assignment of orders higher than five has some degree of uncertainty, both because of the intrinsic difficulty of determining high orders and because, as will be discussed later, some of these ions are formed through different paths.

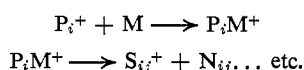
Table IV. Kinetic Orders of Product Ions in Acetylene at 80-V. Electron Beam Energy

Kinetic order							Higher order
2	3	4	5	6	7		
Even-C-number ions							
$C_2H_3^+$	$C_4H_4^+$	$C_4H_5^+$	$C_8H_4^+$	$C_8H_7^+$	$C_{10}H_7^+$	$C_{12}H_9^+$	
C_4H^+	$C_6H_2^+$	$C_6H_4^+$	$C_8H_5^+$	$C_{10}H_6^+$	$C_{10}H_8^+$	$C_{14}H_{11}^+$	
$C_4H_2^+$	$C_6H_3^+$	$C_6H_5^+$	$C_8H_6^+$				
$C_4H_3^+$		$C_8H_2^+$	$C_8H_3^+$				
Odd-C-number ions							
C_3H^+	$C_3H_3^+$	$C_7H_2^+$	$C_7H_4^+$	$C_7H_5^{+a}$	$C_9H_6^+$		
$C_5H_2^+$	$C_5H_3^+$	$C_7H_3^+$		$C_9H_4^+$			
	$C_5H_3^+$			$C_9H_5^+$			

^a The order of this ion is rather uncertain but is definitely higher than five.

Discussion

There are, at present, two different approaches to the problem of the mechanism of ion-molecule reactions occurring in the gas phase inside the ion source of the mass spectrometer. One approach is that used and developed by Lampe, Field, and Franklin,¹⁹ which assumes the formation of a collision complex as the intermediate for the reaction of the ions, as for example P_iM^+ in the reaction sequence



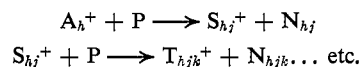
However, in the material formulation of the kinetics of such reactions, Lampe, Field, and Franklin imposed the conditions of steady state on such a collision complex; otherwise, the resulting equations were found to be too involved to be of any practical use.

The other approach is based on Wexler and Jesse's "beam model"^{11,20} which assumes a beam of ions originating at the plane of ionization, and, while it is traveling toward the exit slit, its intensity is attenuated owing to reactions of the ions with the molecules of the gas inside the ion source. This model generally

(19) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. Reaction Kinetics*, 1, 69 (1961).

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

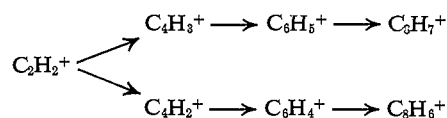
does not assume the formation of any intermediate complex with detectable lifetime, and therefore the reactions are considered as a chain of consecutive steps as in the scheme



So far, both approaches have been applied with equal success and have been found to give essentially equivalent results when applied to ion-molecule reactions occurring in methane^{17,20} and in ethylene.^{18,21}

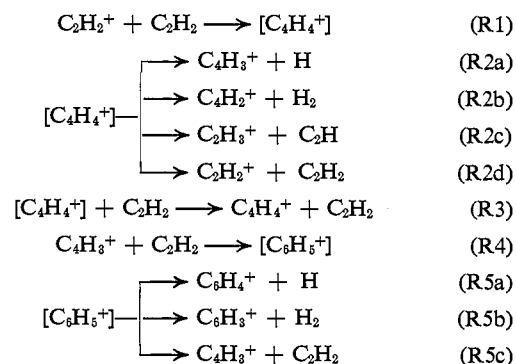
Although there has been no direct experimental evidence supporting one or the other of the two approaches, Lampe, Field, and Franklin have established some interesting correspondence between the secondary mass spectrum of some such "collision complexes" and the primary spectra of their counterpart neutral molecules¹⁹; also recently, Field, Franklin, and Munson¹⁷ have observed some metastable peaks in methane which they interpreted as arising from the decomposition of the collision complex in the analyzer tube of the mass spectrometer.

In acetylene, from the experimental results presented above, the major reaction sequence is

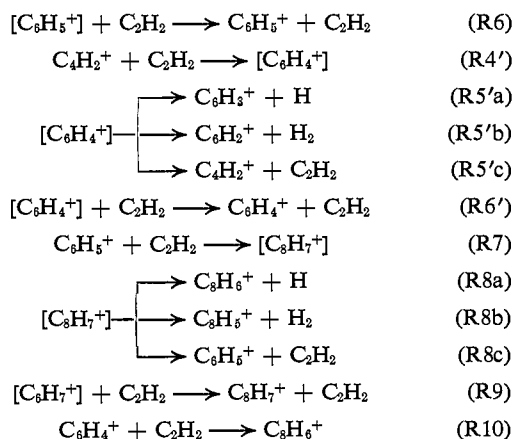


and these results have further established that: (a) the kinetic orders of these ions are (apart from the primary ion $C_2H_2^+$): $C_4H_3^+$ and $C_4H_2^+$, second order; $C_6H_5^+$ and $C_6H_4^+$, fourth order; $C_8H_7^+$, sixth order; $C_8H_6^+$, fifth order; (b) the rates of formation of all possible third-order ions, which may be considered as the precursors of the fourth-order C_6 ions, are much too small to account for the rather large decay in the intensity of the secondary ions $C_4H_3^+$ and $C_4H_2^+$; (c) the two branches of the above sequence are not completely independent of each other, and a number of cross reactions is expected, as may be inferred from the fact that, while the total sum of ion intensities of the ions in the above sequence (apart from $C_2H_2^+$) becomes constant at high pressure, the sum for the upper branch decreases and that for the lower branch increases with pressure at high pressure.

The consequence of points a and b is therefore that the step from the major C_4 ions to the major C_6 ions has to go through the formation of a complex, and not *via* simple, consecutive ion-molecule reactions. Extending to the whole sequence of reactions the collision complex mechanism, one can write the following scheme



(21) F. H. Field, *ibid.*, 83, 1523 (1961).



The prominent feature of the above reaction scheme is the competitive reactions R2 and R3 which involve the unimolecular dissociation of the complex $[\text{C}_4\text{H}_4^+]$ in the former and its stabilization by collision in the latter. Other similar sets of competitive reactions are those involving the complexes $[\text{C}_6\text{H}_4^+]$, $[\text{C}_6\text{H}_5^+]$, and $[\text{C}_8\text{H}_7^+]$.

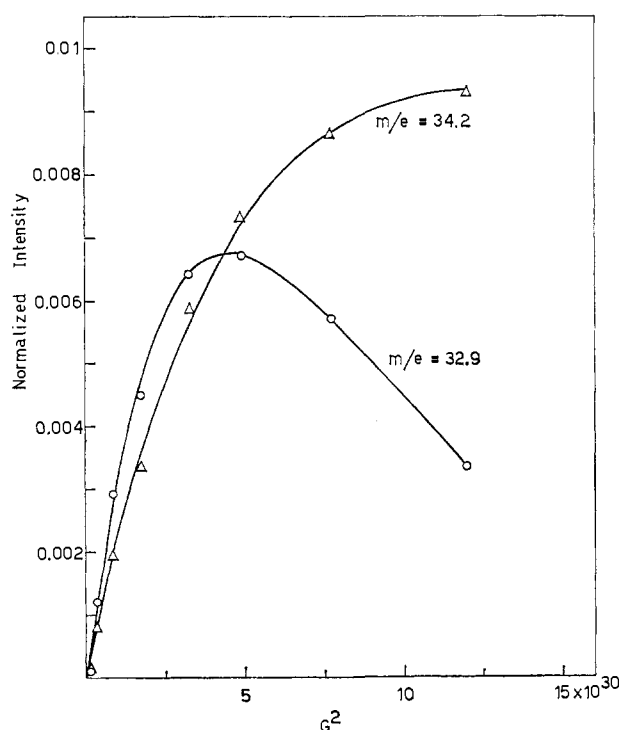


Figure 6. Normalized intensity of the metastable peaks at m/e 32.9 and 34.2 vs. the square of acetylene concentration (15-v. electron beam energy).

One possible check on the above mechanism is to search for metastable peaks which are expected to appear if the collision complexes have long enough lifetimes for some of them to dissociate in the field-free region just before the boundary of the magnetic field inside the analyzer tube. Under the present experimental conditions, the spectrum of acetylene exhibited a number of diffuse peaks at nonintegral mass numbers, and more interesting is the pressure dependence of the intensities of these peaks. Among the metastable peaks observed, the most prominent and well defined are those at mass numbers 32.9 and 34.2

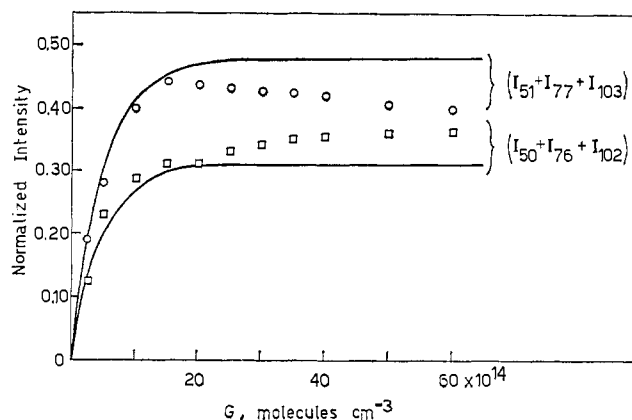


Figure 7. Calculated curves (full lines) and experimental points for the sums of the intensities of the major even-C-number ions in acetylene (80-v. electron beam energy).

which are assigned to the transitions $76 \rightarrow 50$ and $77 \rightarrow 51$, respectively. As is shown in Figure 6, the normalized intensities of these metastable peaks are related to the pressure of the gas by the equation $I_m = \text{constant} \times G^2$, which indicates that they arise from the unimolecular decomposition of $[\text{C}_6\text{H}_4^+]$ and $[\text{C}_6\text{H}_5^+]$, respectively, and not from a collision-induced dissociation of C_6H_4^+ and C_6H_5^+ .

Another interesting metastable peak which behaved in a similar manner is that at mass number 57.5, which is assigned to the transition $103 \rightarrow 77$. These observations give a good measure of support to the proposed mechanism.

In the present work the nonobservation of metastable peaks owing to the unimolecular dissociation of the collision complex $[\text{C}_4\text{H}_4^+]$ may be taken as an indication of the very short lifetime of this ion. Supporting this is the fact that the peak at mass number 52 exhibited a pressure dependence indicative of a third-order ion, and therefore the ion observed may be due to the pressure-stabilization reaction (R3). Of course, the alternative that the ion at m/e 52 is the third-order product of a simple reaction with C_4H_3^+ as the secondary ion precursor cannot be ruled out. Another interesting case is that of the ion at m/e 102 which was found to be only one kinetic order higher than its precursor C_6H_4^+ . This, as well as the nonobservation of metastable peaks owing to transitions involving m/e 102, indicates quite strongly that this ion is a collision complex ion with longer lifetime than the other complexes of the above reaction scheme.

Having established a mechanism for the reactions of even-C-number ions, it is possible to calculate the cross sections of some of the reactions of these ions. These cross sections are calculated from the initial slopes of plots of normalized ion intensity vs. G^{n-1} , where n is the order of the ion, and also from the initial slopes of plots of ion-intensity ratios of related ions vs. G .

The sums $(I_{51} + I_{77} + I_{103})$ and $(I_{50} + I_{76} + I_{102})$ are expected to follow the kinetics of an unreactive secondary ion. In Figure 7 are plotted the calculated curves for these two sums, according to eq. 4 of the Appendix and using the values of cross sections given in Table V. The deviation of the experimental points from the calculated curves indicates the extent of cross

Table V. Cross Sections of Reactions of Even-C-Number Ions in Acetylene

Reaction	Effective cross section ^a
$C_2H_2^+ + C_2H_2 \xrightarrow{\sigma_{26}^T} [C_4H_4^+]$	σ_{26}^T $62 \times 10^{-16} \text{ cm.}^2$
$[C_4H_4^+] + C_2H_2 \xrightarrow{\sigma_{52}^* - 52} C_4H_4^+ + C_2H_2$	$\sigma_{52}^* - 52 \sigma_{26}^T / \sigma_{52}^* T$ $8 \times 10^{-22} \text{ cm.}^5$
$[C_4H_4^+] \xrightarrow{\sigma_{52}^* T} \begin{cases} \xrightarrow{\sigma_{52}^* - 51} C_4H_3^+ + H \\ \xrightarrow{\sigma_{52}^* - 50} C_4H_2^+ + H_2 \\ \xrightarrow{\sigma_{52}^* - 27} C_2H_3^+ + C_2H \end{cases}$	$\sigma_{52}^* - 51 \sigma_{26}^T / \sigma_{52}^* T$ $39 \times 10^{-16} \text{ cm.}^2$ $\sigma_{52}^* - 50 \sigma_{26}^T / \sigma_{52}^* T$ $22 \times 10^{-16} \text{ cm.}^2$ $\sigma_{52}^* - 27 \sigma_{26}^T / \sigma_{52}^* T$ $0.1 \times 10^{-16} \text{ cm.}^2$
$C_2H^+ + C_2H_2 \xrightarrow{\sigma_{25}^T} [C_4H_3^+]$	σ_{25}^T $70 \times 10^{-16} \text{ cm.}^2$
$[C_4H_3^+] \xrightarrow{\sigma_{51}^* T} \begin{cases} \xrightarrow{\sigma_{51}^* - 50} C_4H_2^+ + H \\ \xrightarrow{\sigma_{51}^* - 49} C_4H^+ + H_2 \\ \xrightarrow{\sigma_{51}^* - 27} C_2H_3^+ + C_2 \end{cases}$	$\sigma_{51}^* - 50 \sigma_{25}^T / \sigma_{51}^* T$ $25 \times 10^{-16} \text{ cm.}^2$ $\sigma_{51}^* - 49 \sigma_{25}^T / \sigma_{51}^* T$ $10 \times 10^{-16} \text{ cm.}^2$ $\sigma_{51}^* - 27 \sigma_{25}^T / \sigma_{51}^* T$ $18 \times 10^{-16} \text{ cm.}^2$
$C_2^+ + C_2H_2 \xrightarrow{\sigma_{24}^T} [C_4H_2^+]$	σ_{24}^T $72 \times 10^{-16} \text{ cm.}^2$
$[C_4H_2^+] \xrightarrow{\sigma_{50}^* T} \begin{cases} \xrightarrow{\sigma_{50}^* - 49} C_4H^+ + H \\ \xrightarrow{\sigma_{50}^* - 38} C_3H_2^+ + C \end{cases}$	$\sigma_{50}^* - 49 \sigma_{24}^T / \sigma_{50}^* T$ $29 \times 10^{-16} \text{ cm.}^2$ $\sigma_{50}^* - 38 \sigma_{24}^T / \sigma_{50}^* T$ $41 \times 10^{-16} \text{ cm.}^2$
$C_4H_3^+ + C_2H_2 \xrightarrow{\sigma_{51}^T} [C_6H_5^+]$	σ_{51}^T $18 \times 10^{-16} \text{ cm.}^2$
$[C_6H_5^+] + C_2H_2 \xrightarrow{\sigma_{77}^* - 77} C_6H_5^+ + C_2H_2$	$\sigma_{77}^* - 77 \sigma_{51}^T / \sigma_{77}^* T$ $25 \times 10^{-22} \text{ cm.}^5$
$[C_6H_5^+] \xrightarrow{\sigma_{77}^* - 75} C_6H_3^+ + H_2$	$\sigma_{77}^* - 75 \sigma_{51}^T / \sigma_{77}^* T$ $4 \times 10^{-16} \text{ cm.}^2$
$C_4H_2^+ + C_2H_2 \xrightarrow{\sigma_{50}^T} [C_6H_4^+]$	σ_{50}^T $33 \times 10^{-16} \text{ cm.}^2$
$[C_6H_4^+] + C_2H_2 \xrightarrow{\sigma_{76}^* - 76} C_6H_4^+ + C_2H_2$	$\sigma_{76}^* - 76 \sigma_{50}^T / \sigma_{76}^* T$ $68 \times 10^{-22} \text{ cm.}^5$
$C_2H_3^+ + C_2H_2 \xrightarrow{\sigma_{27}^T} [C_4H_5^+]$	σ_{27}^T $20 \times 10^{-16} \text{ cm.}^2$
$[C_4H_5^+] + C_2H_2 \xrightarrow{\sigma_{53}^* - 53} C_4H_5^+ + C_2H_2$	$\sigma_{53}^* - 53 \sigma_{27}^T / \sigma_{53}^* T$ $7 \times 10^{-22} \text{ cm.}^5$
$[C_4H_5^+] \xrightarrow{\sigma_{53}^* - 39} C_4H_3^+ + CH_2$	$\sigma_{53}^* - 39 \sigma_{27}^T / \sigma_{53}^* T$ $8 \times 10^{-16} \text{ cm.}^2$
$C_4H^+ + C_2H_2 \xrightarrow{\sigma_{49}^T} [C_6H_3^+]$	σ_{49}^T ...
$[C_6H_3^+] \xrightarrow{\sigma_{75}^* - 74} C_6H_2^+ + H$	$\sigma_{75}^* - 74 \sigma_{49}^T / \sigma_{75}^* T$ $100 \times 10^{-16} \text{ cm.}^2$
$C_6H_2^+ + C_2H_2 \xrightarrow{\sigma_{74}^T} [C_8H_4^+]$	σ_{74}^T ...
$[C_8H_4^+] + C_2H_2 \xrightarrow{\sigma_{100}^* - 100} C_8H_4^+ + C_2H_2$	$\sigma_{100}^* - 100 \sigma_{74}^T / \sigma_{100}^* T$ $8 \times 10^{-22} \text{ cm.}^5$
$C_6H_4^+ + C_2H_2 \xrightarrow{\sigma_{76} - 102} C_8H_6^+$	$\sigma_{76} - 102$ $1 \times 10^{-16} \text{ cm.}^2$

^a The significance of these cross sections is explained in the Appendix.

reactions between these two series and further shows that such mixing is mainly due to ions 51 and 77 reacting to give ions 76 and 102, respectively, as indicated in (R5a) and (R8a). In the calculation for the $C_4H_2^+$ branch, the contribution of C_2H^+ is taken into account (see Table V).

Both $C_4H_3^+$ and $C_4H_2^+$ show considerable decay at high pressure, and, since the ratios I_{51}/I_{26} and I_{50}/I_{36} vary with gas concentration in the manner of a secondary ion of less reactivity than its primary ion precursor, the total cross sections of decay of these two ions may be calculated from the slope of the decay part of the semilogarithmic plot of ion intensity vs. G .

The values so obtained for the total cross sections of reactions of $C_4H_3^+$ and $C_4H_2^+$ are 18 and $33 \times 10^{-16} \text{ cm.}^2 \text{ molecule}^{-1}$, respectively. Using the values of cross sections of formation of $C_4H_3^+$ and $C_4H_2^+$ together with the above values for their decay cross sections, it is now possible to calculate the pressure dependence curves for the intensities of these ions from eq. 4. The results are shown in Figure 8 where the internal consistency of the treatment is evident.

Besides the two major reaction sequences of $C_4H_3^+$ and $C_4H_2^+$, there are two other minor sequences of even-C-number ions. These are

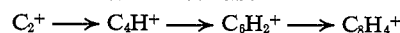
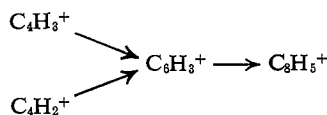


Table VI. Cross Sections of Reactions of Odd-C-Number Ions in Acetylene

Reaction	Effective cross section ^a
$\text{CH}^+ + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{18}^{\tau}} [\text{C}_3\text{H}_3^+]$	σ_{18}^{τ} $45 \times 10^{-16} \text{ cm.}^2$
$[\text{C}_3\text{H}_3^+] \xrightarrow{\sigma_{39}^{*-37}} \text{C}_3\text{H}^+ + \text{H}_2$	$\sigma_{39}^{*-37} \sigma_{18}^{\tau} / \sigma_{39}^{*\tau}$ $25 \times 10^{-16} \text{ cm.}^2$
$\text{C}^+ + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{12}^{\tau}} [\text{C}_3\text{H}_2^+]$	σ_{12}^{τ} $45 \times 10^{-16} \text{ cm.}^2$
$[\text{C}_3\text{H}_2^+] \xrightarrow{\sigma_{38}^{*-37}} \text{C}_3\text{H}^+ + \text{H}$	$\sigma_{38}^{*-37} \sigma_{12}^{\tau} / \sigma_{38}^{*\tau}$ $25 \times 10^{-16} \text{ cm.}^2$
$\text{C}_3\text{H}^+ + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{37}^{\tau}} [\text{C}_5\text{H}_3^+]$	σ_{37}^{τ} ...
$[\text{C}_5\text{H}_3^+] \xrightarrow{\sigma_{68}^{*-62}} \text{C}_5\text{H}_2^+ + \text{H}$	$\sigma_{68}^{*-62} \sigma_{37}^{\tau} / \sigma_{68}^{*\tau}$ $60 \times 10^{-16} \text{ cm.}^2$
$\text{C}_3\text{H}_2^+ + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{38}^{\tau}} [\text{C}_6\text{H}_4^+]$	σ_{38}^{τ} ...
$[\text{C}_6\text{H}_4^+] \xrightarrow{\sigma_{64}^{*-63}} \text{C}_5\text{H}_3^+ + \text{H}$	$\sigma_{64}^{*-63} \sigma_{38}^{\tau} / \sigma_{64}^{*\tau}$ $36 \times 10^{-16} \text{ cm.}^2$
$\text{C}_6\text{H}_2^+ + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{62}^{\tau}} [\text{C}_7\text{H}_4^+]$	σ_{62}^{τ} ...
$[\text{C}_7\text{H}_4^+] + \text{C}_2\text{H}_2 \xrightarrow{\sigma_{88}^{*-88}} \text{C}_7\text{H}_4^+ + \text{C}_2\text{H}_2$	$\sigma_{88}^{*-88} \sigma_{62}^{\tau} / \sigma_{88}^{*\tau}$ $8 \times 10^{-32} \text{ cm.}^4$

^a The significance of these cross sections is explained in the Appendix.

and



For the upper sequence the sum ($I_{49} + I_{74} + I_{100}$) reaches a constant value at a gas concentration of 10×10^{14} molecules cm.^{-3} , but for the lower sequence it is not possible to carry out such a summation since this sequence is, in fact, a minor branch of C_4H_3^+ and C_4H_2^+ main reaction paths.

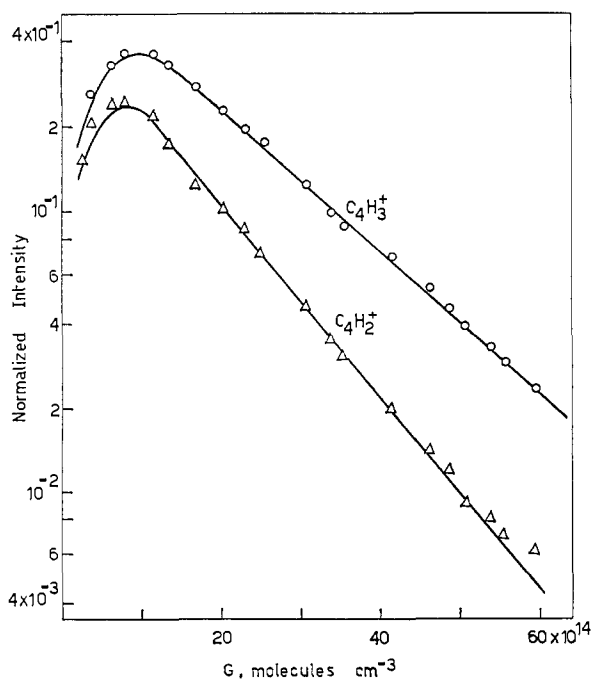
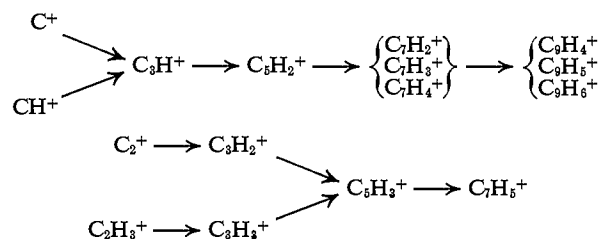


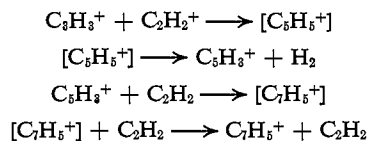
Figure 8. Semilogarithmic plots of calculated curves (full lines) and experimental points for the intensities of the secondary ions C_4H_3^+ and C_4H_2^+ (80-v. electron beam energy).

The major reaction sequences for the odd-C-number ions are



For these sequences, the sums ($I_{37} + I_{62} + I_{86} + I_{87} + I_{88} + I_{112} + I_{113} + I_{114}$) and ($I_{38} + I_{27} + I_{39} + I_{63} + I_{89}$) are found to approach constant values at gas concentrations larger than 12×10^{14} molecules cm.^{-3} .

As in the case of even-C-number ions, cross reactions between odd-C-number ions are also expected, but the generally low intensities of these ions make it difficult to evaluate the extent of such reactions. Such cross reactions in many cases give rise to a common product ion of differing kinetic orders dependent on its path of formation, as for example in the case of C_5H_3^+ . It is interesting to note that, while C_5H_3^+ is a third-order ion at 80-v. electron energy as expected if it is formed from C_3H_2^+ , C_7H_5^+ is an ion of an order higher than five. This may be explained by considering its formation through the reactions

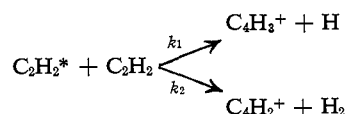


Such a scheme may also account for the formation of C_5H_3^+ and C_7H_5^+ at a 15-v. electron beam energy where C_5H_3^+ is found to be a fourth-order ion. This scheme further explains the low intensity C_5H_5^+ which may be formed as the product of collision stabilization of the complex $[\text{C}_5\text{H}_5^+]$.

Conclusion

The analysis of the results obtained in the present work adds some interesting evidence to the presence of "collision complexes" of considerable lifetime in ion-molecule reactions as was shown by the mechanism of formation of the major product ions $C_6H_4^+$ and $C_6H_5^+$. The conventional mass spectrometric technique used in the kinetic study of ion-molecule reactions does not allow for a clear distinction between the "collision complex" mechanism and the simple consecutive reactions mechanism. Thus, the unimolecular decomposition of the "collision complex" mainly in an ion different from the precursor could not be clearly distinguished from a series of consecutive reactions which does not consider the presence of such complexes. This has been demonstrated unequivocally in the case of ethylene^{18,21} where both mechanisms have adequately explained the main features of the kinetics of ion-molecule reactions.

The ionic reactions in acetylene have been discussed so far in terms of simple primary ions without taking into account the role of excited ions or excited molecules. Recently, evidence has been put forward indicating the important contribution of such species. Koyano, Tanaka, and Omura²² have found direct evidence for the chemionization reactions



with $k_1/k_2 = 1.25$. The importance of such reactions in the present study cannot be underestimated, but, at present, there is no possibility of separating the processes leading to the formation of $C_4H_3^+$ and $C_4H_2^+$ via primary ions and via excited molecules.

The evidence for excited $C_2H_2^+$ has been put forward by Lindholm, Szabo, and Wilmenius.⁷ These authors have found that there are two states of $C_2H_2^+$, the low energy ion leading by ion-molecule reactions to the formation of $C_4H_3^+$ and the high energy ion leading to the formation of $C_4H_2^+$. Because, however, the threshold of formation of the high energy ion lies very close to that for the formation of C_2H^+ , it is not possible with the present experiments to identify the nature of the primary ion.²³ The mechanism used previously can only be considered, therefore, as a simplification. Furthermore, the possibility of detecting different total cross sections of decay for the different $C_2H_2^+$ ions is completely overshadowed by the experimental trouble at high pressures where the decay curves of primary ions exhibit tails extending over a wide pressure range (Figure 2). If, however, the suspected role of excited ions and excited molecules throws some doubts on the picture given above for the formation of C_4 ions, it should not affect the processes producing higher C_n ions.

Of particular interest is the bearing which the present results have on the radiolysis of acetylene. It is in-

(22) I. Koyano, I. Tanaka, and I. Omura, *J. Chem. Phys.*, 40, 2734 (1964).

(23) After they had submitted the present paper for publication, the authors noticed that more direct and detailed evidence of different types of acetylene ions reacting to give $C_4H_2^+$ and $C_4H_3^+$ had been presented by C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, 41, 1469 (1964).

teresting to note that the high reactivity of all ions in acetylene is a strong support toward an ionic mechanism for the radiation-induced polymerization of acetylene leading to the formation of cuprene. Even the interpretation that benzene is formed via radical mechanism in the radiolysis of acetylene finds a good measure of support in the present study. In fact, the major C_6 ions react fairly rapidly to form higher ions so that it is very unlikely that they can give benzene by neutralization or by charge-exchange processes. The only C_6 ion which seemed very unreactive is $C_6H_6^+$, but it is formed in very low yield.

Acknowledgments. We are indebted to Emilio Luzzatti of this laboratory for carrying out the experimental measurements with his usual skill and competence. G. A. W. D. wishes to thank Consiglio Nazionale delle Ricerche for a fellowship.

Appendix

In this section it is proposed to develop the mathematical equations for the intensities of a representative number of ions of the reaction scheme (R1)-(R10) presented in this work for the mechanism of ion-molecule reactions in acetylene. In these calculations the "beam model" will be used, but with the formation and further reaction of the collision complex ion being taken into account.

Calculations for $[C_4H_4^+]$, $C_4H_3^+$, and $C_4H_4^+$. The equation for the intensity of the primary ion is simply

$$I_{26} = I_{26}^0 \exp(-\sigma_{26} \tau l G) \quad (1)$$

For the collision complex $[C_4H_4^+]$, the intensity I_{52}^* is given by

$$I_{52}^* = \frac{\sigma_{26} \tau I_{26}^0 G}{(\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G) - \sigma_{26} \tau G} \{ \exp(-\sigma_{26} \tau l G) - \exp[-(\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G) l] \} \quad (2)$$

Equation 2 is obtained without the assumption of steady state. However, when it is used for the calculations of the other ions, the resulting expressions are too cumbersome to be of any use. Assuming steady-state conditions for $[C_4H_4^+]$, one obtains

$$I_{52}^* = \frac{\sigma_{26} \tau I_{26}^0 G}{\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G} \quad (3)$$

With the use of eq. 3, relatively simple expressions for I_{51} and I_{52} are obtained

$$I_{51} = \frac{\sigma_{52}^* - \sigma_{51} \sigma_{26} \tau I_{26}^0 G}{(\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G)(\sigma_{51} \tau - \sigma_{26} \tau)} \{ \exp(-\sigma_{26} \tau l G) - \exp(-\sigma_{51} \tau l G) \} \quad (4)$$

$$I_{52} = \frac{\sigma_{52}^* - \sigma_{52} \sigma_{26} \tau I_{26}^0 G}{(\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G)(\sigma_{52} \tau - \sigma_{26} \tau)} \{ \exp(-\sigma_{26} \tau l G) - \exp(-\sigma_{52} \tau l G) \} \quad (5)$$

Equation 4 is essentially the same as the one derived previously¹¹ for the intensity of a secondary ion without assuming the formation of an intermediate collision complex. Thus, in the pre-exponential factor the "effective cross section" of formation of the secondary ion is given by $\sigma_{52}^* - \sigma_{51} \sigma_{26} \tau / (\sigma_{52}^* \tau + \sigma_{52}^* - \sigma_{52} G)$ which at very low pressures assumes the simple form $\sigma_{52}^* - \sigma_{51} \sigma_{26} \tau / \sigma_{52}^* \tau$.

In the low pressure range eq. 4 and 5 may be simplified by expanding the exponential terms in series. The resulting equations are

$$I_{51} = \frac{\sigma_{52^*} \sigma_{26} I_{26}^0}{(\sigma_{52^*} + \sigma_{52^*-52} G)} G \quad (4a)$$

and

$$I_{52} = \frac{\sigma_{52^*} \sigma_{26} I_{26}^0}{(\sigma_{52^*} + \sigma_{52^*-52} G)} G^2 \quad (5a)$$

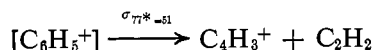
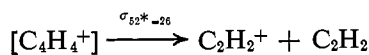
which may be used to calculate the "effective cross sections" of formation of these ions, thus

$$\frac{\sigma_{52^*} \sigma_{26}}{\sigma_{52^*}} = \frac{1}{I_{26}^0} \left[\frac{dI_{51}}{dG} \right]_{G=0} \quad (6)$$

$$\frac{\sigma_{52^*} \sigma_{26}}{\sigma_{52^*}} = \frac{1}{I_{26}^0} \left[\frac{dI_{51}}{dG} \right]_{G=0} \left[\frac{d(I_{52}/I_{51})}{dG} \right]_{G=0} \quad (7)$$

For the calculation of the cross sections of decay of these ions (*i.e.*, σ_{51}^{τ} and σ_{52}^{τ}) use may be made of the same general method which has been developed previously.¹¹

In the above calculations, the back reactions



have not been considered. It can be shown that, when these reactions are introduced in the calculations, the resulting equations will be essentially the same as eq. 1 and 4 with σ_{26}^{τ} replaced by

$$\sigma_{26}^{\tau} \left\{ 1 - \frac{\sigma_{52^*-26}}{(\sigma_{52^*} + \sigma_{52^*-52} G)} \right\}$$

and σ_{51}^{τ} replaced by

$$\sigma_{51}^{\tau} \left\{ 1 - \frac{\sigma_{77^*-51}}{(\sigma_{77^*} + \sigma_{77^*-77} G)} \right\}$$

The importance of the correction terms inside the braces has to be judged by the extent of the forward reactions of the respective ions. Also, since the gas concentration occurs in the denominator, these correction terms become progressively insignificant at high gas concentrations.

Calculations for $[C_6H_5^+]$, $C_6H_5^+$, and $C_6H_3^+$. Assuming that steady-state conditions are applicable for

$[C_6H_5^+]$, one obtains

$$I_{77^*} = \frac{\sigma_{51}^{\tau} G I_{51}}{(\sigma_{77^*} + \sigma_{77^*-77} G)} \quad (8)$$

which, when introduced into the calculations for $C_6H_5^+$ and $C_6H_3^+$, formed by (R6) and (R5b), respectively, gives the resulting equations

$$I_{77} = \frac{\sigma_{77^*-77} \sigma_{52^*-51} \sigma_{51}^{\tau} \sigma_{26} I_{26}^0 G}{(\sigma_{52^*} + \sigma_{52^*-52} G)(\sigma_{77^*} + \sigma_{77^*-77} G)} \times \left\{ \frac{\exp(-\sigma_{26}^{\tau} l G)}{(\sigma_{51}^{\tau} - \sigma_{26}^{\tau})(\sigma_{77^*} - \sigma_{26}^{\tau})} + \frac{\exp(-\sigma_{51}^{\tau} l G)}{(\sigma_{26}^{\tau} - \sigma_{51}^{\tau})(\sigma_{77^*} - \sigma_{51}^{\tau})} + \frac{\exp(-\sigma_{77}^{\tau} l G)}{(\sigma_{26}^{\tau} - \sigma_{77}^{\tau})(\sigma_{51}^{\tau} - \sigma_{77}^{\tau})} \right\} \quad (9)$$

and

$$I_{75} = \frac{\sigma_{77^*-75} \sigma_{52^*-51} \sigma_{51}^{\tau} \sigma_{26} I_{26}^0}{(\sigma_{52^*} + \sigma_{52^*-52} G)(\sigma_{77^*} + \sigma_{77^*-77} G)} \times \left\{ \frac{\exp(-\sigma_{26}^{\tau} l G)}{(\sigma_{51}^{\tau} - \sigma_{26}^{\tau})(\sigma_{75}^{\tau} - \sigma_{26}^{\tau})} + \frac{\exp(-\sigma_{51}^{\tau} l G)}{(\sigma_{26}^{\tau} - \sigma_{51}^{\tau})(\sigma_{75}^{\tau} - \sigma_{51}^{\tau})} + \frac{\exp(-\sigma_{75}^{\tau} l G)}{(\sigma_{26}^{\tau} - \sigma_{75}^{\tau})(\sigma_{51}^{\tau} - \sigma_{75}^{\tau})} \right\} \quad (10)$$

Equations 9 and 10 are too complicated to be of any direct use. However, in the range of low pressure, they may be simplified to give

$$I_{77} = \frac{\sigma_{77^*-77} \sigma_{52^*-51} \sigma_{51}^{\tau} \sigma_{26} I_{26}^0}{(\sigma_{52^*} + \sigma_{52^*-52} G)(\sigma_{77^*} + \sigma_{77^*-77} G)} \times \frac{l^2 G^3}{2} \quad (11)$$

$$I_{75} = \frac{\sigma_{77^*-75} \sigma_{52^*-51} \sigma_{51}^{\tau} \sigma_{26} I_{26}^0}{(\sigma_{52^*} + \sigma_{52^*-52} G)(\sigma_{77^*} + \sigma_{77^*-77} G)} \times \frac{l^2 G^2}{2} \quad (12)$$

It is quite clear by now that only the low pressure, approximate equations can be of any use for the higher order ions, and these equations are in general very similar to (11) and (12) and can easily be derived.

It must be mentioned at this stage that what one hopes to achieve for the higher order ions is nothing more than a semiquantitative account of their kinetic behavior. However full calculations of the intensities of such ions at various values of gas concentration and comparison of these calculations with experimental data cannot be expected to give any meaningful information owing to the rather large number of parameters involved, especially the cross sections for unimolecular dissociations of collision complexes, for which no data are available at the present.