

The failure of ethylene, propylene, and ammonia to trap electrons, although several other olefins and triethylamine do so, cannot be explained. We can only observe that these molecules all have fairly high ionization potentials relative to their analogs which were found to be effective. This suggests that trapping the positive hole by solute in 3MP is prerequisite to anion stability, but this assumption appears to be inconsistent with  $G(\text{C}_{12}\text{H}_{10}^-) = 1.57$  for 0.15% biphenyl in 3MP.

It is usually assumed that charge transfer from solvent to solute will occur only when the ground state ionization potential of the solvent is greater than that of the solute. The frequent observation and identification of solute cations in good yields from various alkene, aromatic, and amine compounds having lower ionization potentials than 3MP supports this view. However, small concentrations of various alkyl halides pro-

duce cations although their ionization and appearance potentials exceed those of 3MP. The best studied example is carbon tetrachloride.<sup>10</sup> The ion  $\text{CCl}_4^+$  cannot be detected in a mass spectrometer at pressures several times greater than normal and the appearance potential of  $\text{CCl}_3^+$  is 11.65 e.v.<sup>11</sup> It may be that some solvent cations are produced in excited states, which could then account for these results. There is extensive evidence from mass spectrometry for ionic excitation<sup>12</sup> and no evident reason to exclude this possibility in condensed phases.

(10) S. Leach and R. Lopez-Delgado have recently reported (*Compt. rend.*, **266**, 1299 (1963)) observing a color center produced by ultraviolet excitation of benzene in 7% carbon tetrachloride in alkane glass. They follow our original suggestion that  $\text{CCl}_4^-$  is responsible.

(11) J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

(12) C. E. Melton and W. H. Hamill, unpublished results.

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## Consecutive Ion-Molecule Reactions in Ethylene<sup>1</sup>

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Reactions of positive ions with ethylene molecules have been studied at pressures up to a few tenths of a millimeter in the source chamber of a mass spectrometer. Confirming earlier studies with different procedures, the data show that increasingly heavy polymeric ions appear to be formed in chains of consecutive reactions between ions and  $\text{C}_2\text{H}_4$  molecules. Some specific chains of such reactions are suggested. The sequence involving the ions  $\text{C}_2\text{H}_4^+$ ,  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_5\text{H}_9^+$ , and  $\text{C}_7\text{H}_{13}^+$  is the dominant mechanism for the initial propagation of ionic polymerization of ethylene at low pressure in the gas phase. Cross sections for the reactions of primary and secondary ions with  $\text{C}_2\text{H}_4$  have been estimated from the concentration dependences of the intensities of the ionic species. The mass spectrometric results found by us and others are correlated with the observations on the radiolysis of ethylene.

Several investigators have used conventional techniques to study the radiolysis of gaseous ethylene at pressures ranging from 10 to 1000 mm.<sup>2a,b</sup> The main radiolytic products are acetylene and hydrogen, but they account for only about 10% of the  $\text{C}_2\text{H}_4$  destroyed. The remainder is converted to products higher in molecular weight, mainly polymer.<sup>3</sup> To understand some of the mechanisms of gas-phase radiolysis of  $\text{C}_2\text{H}_4$ , we have used techniques of "high pressure" mass spectrometry<sup>4</sup> to investigate ionic reactions in this gas. Field,<sup>5</sup> who ionized the gas with an electron beam, as well as Melton and Rudolph,<sup>6</sup> who employed a  $\text{Po}^{208}$   $\alpha$ -source as the ionizing agent, have already identified ionic reactions in ethylene at relatively high pressures in the source chambers of their mass spectrometers; but their approaches, both experimental and theoretical, differ considerably from ours. Comparison of the results, particularly of reaction mechanisms and cross sections, is therefore worthwhile. In additional contrast to the efforts of these workers, who were mainly interested in ionic reaction mechanisms *per se*, we have attempted to correlate the mass spectrometric results with those obtained from radiolysis studies. Thus the "high pressure" experiments may be regarded as an effort to bridge at least partially the gap between kinetic experiments at ordinary pressures and low-pressure studies on the primary events of excitation and ionization by radiation.

### A. Experimental

The mass spectrometer used in this work has been described previously.<sup>4,7</sup> Two different designs of the source were used in the measurements on  $\text{C}_2\text{H}_4$ . Source 1, employed in earlier work, admitted the electrons through a hole 0.001 in. in diameter and had a slot measuring 0.001  $\times$  0.080 in. for exit of the ions. The repeller was hemicylindrical in shape. The pressure in this source chamber was determined by calculation from the measured pressure in the gas reservoir. Experience with this source led to construction of an improved assembly, source 2 (Fig. 1). The side tube and double ring seal provide for direct measurement of the pressure in the chamber. The pressure was measured by a calibrated dual-range McLeod gage. The electron beam, collimated by aligned slits, enters the chamber through a 0.003  $\times$  0.040 in. slot, while the exit slot for the positive ions is 0.003  $\times$  0.080 in. The electrons travel parallel to the length of the ion exit slit. The repeller is a flat plate. The ionizing current of electrons (energy = 144 e.v.) in this source is much lower than that used by other workers; when the filament emission is 250  $\mu\text{a}$ ., the trap current is only 0.02  $\mu\text{a}$ .. Thermocouples welded to opposite corners of the chamber recorded a temperature of  $122 \pm 2^\circ$  with current flowing through the electron-emitting filament. The mean distance between the plane of the ionizing electron beam and the plane of the ion slit is estimated to be 3.2 mm.

The Phillips research grade  $\text{C}_2\text{H}_4$  (99.84%) used in these experiments was further purified by repeated condensation in liquid nitrogen and pumping with a mercury diffusion pump.

The procedure was in general the same as that employed in the studies on methane,<sup>4</sup> except for the improvement that the rather large amount of data was processed by the IBM-704 computer at this laboratory.

### B. Results

1. "High Pressure" Mass Pattern of  $\text{C}_2\text{H}_4$ .—In sharp contrast to the relatively simple mass spectra of primary ions observed on electron impact of ethylene at low pressures ( $\approx 10^{-5}$ – $10^{-6}$  mm.), a very extensive pattern of singly-charged ions is found at a source pressure of 0.20 mm. The data given in Table I come from source 2; but a fairly similar pattern is

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

(2) (a) M. C. Sauer, Jr., and L. M. Dorfman, *J. Phys. Chem.*, **66**, 322 (1962); (b) P. Ausloos and R. Gordon, Jr., *J. Chem. Phys.*, **36**, 5 (1962). References to earlier literature are given in these references.

(3) F. W. Lampe, *Radiation Research*, **10**, 691 (1959); J. C. Hayward and R. H. Bretton, *Chem. Eng. Progr. Symp. Ser.*, **50** (13), 73 (1954); S. C. Lind and G. Glockler, *J. Am. Chem. Soc.*, **52**, 4450 (1930).

(4) S. Wexler and N. Jesse, *ibid.*, **84**, 3425 (1962); S. Wexler, *ibid.*, **85**, 272 (1963).

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

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

(7) S. Wexler and N. Jesse, Argonne National Laboratory Report ANL-6376 (June, 1961), p. 23 (unpublished).

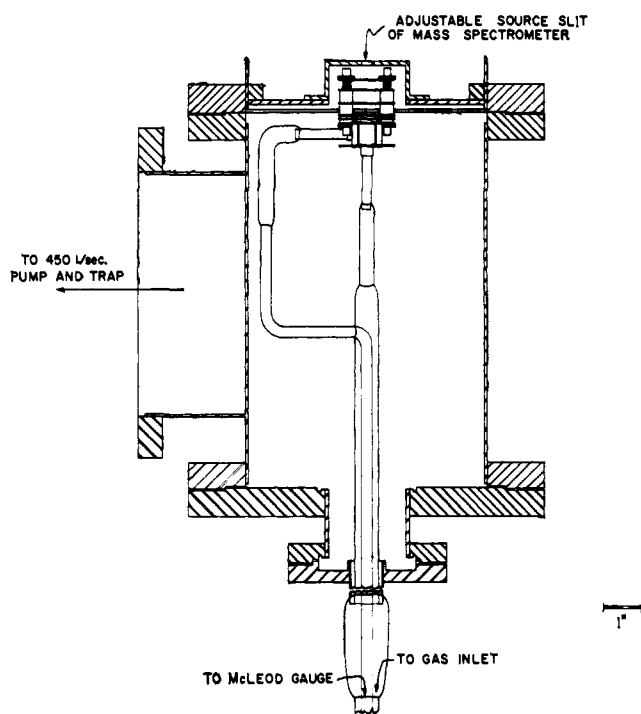


Fig. 1.—Source assembly (source 2) for high-pressure studies on ethylene.

found at comparable gas concentrations in source 1. The results agree qualitatively with the complex pattern also obtained by Field<sup>5</sup> for a source pressure of 0.21 mm. and a mean primary ion path of 2.0 mm.,

TABLE I  
MASS SPECTRUM OF  $C_2H_4$  AT 0.20 MM. PRESSURE (SOURCE 2)

$m/e$	Probable species	Rel. abundance ( $C_2H_4^+ = 100$ ) <sup>a</sup>	$m/e$	Probable species	Ref. abundance ( $C_2H_4^+ = 100$ ) <sup>a</sup>
12	C	<1	57	$C_4H_9$	1,940
13	CH	<1	58	$C_4H_{10}$	<1
14	$CH_2$	<1	63	$C_5H_3$	12
24.3	<sup>b</sup>	85	65	$C_5H_5$	58
25	$C_2H$	<1	66	$C_5H_6$	24
26	$C_2H_2$	24	67	$C_5H_7$	1,000
27	$C_2H_3$	69	68	$C_5H_8$	70
28	$C_2H_4$	100	69	$C_5H_9$	21,200
29	$C_2H_5$	233	70	$C_5H_{10}$	90
30	$C_2H_6$	2	71	$C_5H_{11}$	173
36	$C_3$	6	72	$C_5H_{12}$	2
37	$C_3H$	<1	77	$C_6H_5$	20
38	$C_3H_2$	<1	78	$C_6H_6$	19
39	$C_3H_3$	1840	79	$C_6H_7$	410
40	$C_3H_4$	29	80	$C_6H_8$	5
41	$C_3H_5$	1760	81	$C_6H_9$	460
42	$C_3H_6$	<1	82	$C_6H_{10}$	4
43	$C_3H_7$	42	83	$C_6H_{11}$	1,190
50	$C_4H_2$	<1	84	$C_6H_{12}$	113
51	$C_4H_3$	<1	85	$C_6H_{13}$	36
52	$C_4H_4$	62	91	$C_7H_7$	22
53	$C_4H_5$	1080	97	$C_7H_{13}$	370
54	$C_4H_6$	88	103	$C_8H_7$	29
55	$C_4H_7$	700	105	$C_8H_9$	49
56	$C_4H_8$	2140			

<sup>a</sup> The intensity of each species has been corrected for naturally occurring  $C^{13}$ . <sup>b</sup> The ion peak near mass 24 is broad. It is probably the product from fragmentation of a metastable  $C_2H_4^+$  ion.

except that the extent of reaction in our experiments appears to be greater (sometimes much greater). Because of the reduced sensitivity and differing ionizing

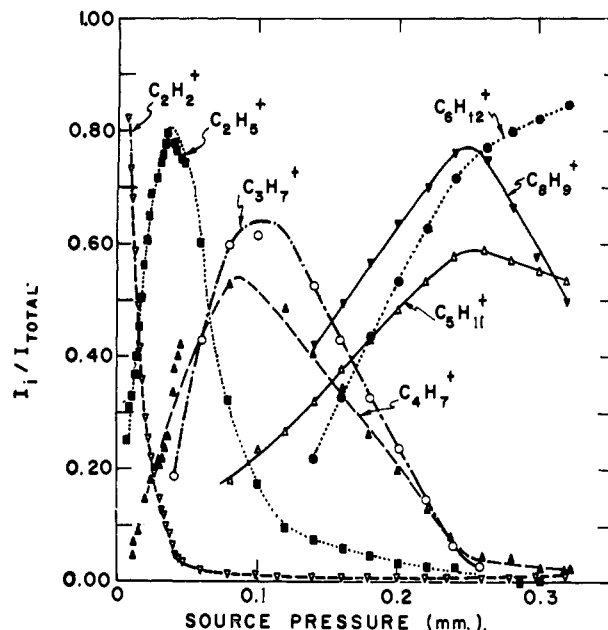


Fig. 2.—Behavior of normalized intensities of various ionic species with increasing pressure of  $C_2H_4$  in source chamber. The scale factors of the fractional intensities are  $2 \times 10^{-1}$  for  $C_2H_2^+$ ,  $2 \times 10^{-1}$  for  $C_2H_5^+$ ,  $5 \times 10^{-3}$  for  $C_3H_7^+$ ,  $10^{-1}$  for  $C_4H_7^+$ ,  $10^{-2}$  for  $C_5H_{11}^+$ ,  $10^{-2}$  for  $C_6H_{12}^+$ , and  $2 \times 10^{-3}$  for  $C_8H_9^+$ .

medium, the mass pattern observed by Melton and Rudolph<sup>6</sup> is considerably simpler than that shown in Table I. But the more prominent species observed by us are the same as were found by them. One notes that at this gas concentration the secondary and tertiary ions dominate the spectrum, the polymeric species  $C_5H_9^+$  being by far the most prominent. At this source pressure  $C_5H_9^+$ , a tertiary ion, accounts for 60% of the total ion intensity. Species through mass 105 are recorded. There may very well be ions of higher weight, as observed by Field, but they were not searched for. The data indicate a low degree of gas-phase polymerization resulting from consecutive ion-molecule reactions.

Intensities relative to  $C_2H_4^+$  (intensity = 100) such as are listed in Table I apply only at the stated pressure; like the studies on methane<sup>4</sup> and the results of Field and of Rudolph and Melton, the normalized intensities (the intensity of the ion divided by the total intensity of all ions) of the various species vary strongly with the concentration of  $C_2H_4$  in the source chamber. The yields of primary ions ( $C_2H_4^+$ ,  $C_2H_3^+$ ,  $C_2H_2^+$ ,  $C_2H^+$ ,  $CH_2^+$ , and  $CH^+$ ) appear to decrease exponentially with pressure, while those of secondary ions formed by reaction of primaries with  $C_2H_4$  molecules (e.g.,  $C_2H_5^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H_7^+$ ) increase to a maximum and then decrease roughly exponentially. The species with  $m/e = 24.3$  behaves as though it is formed both directly by electron impact followed by unimolecular dissociation and as a product of the collision of an ion with  $C_2H_4$ . The broadness and nonintegral mass position of the peak indicates that it is probably due to the dissociation of metastable  $C_2H_4^+$  ions to  $C_2H_2^+ + H_2$ . The tertiary entities (e.g.,  $C_5H_7^+$ ,  $C_5H_9^+$ ,  $C_5H_{10}^+$ ,  $C_6H_7^+$ ,  $C_6H_9^+$ ) increase in intensity to a plateau and then decrease only slightly in the range of pressures (0.005 to 0.32 mm.) studied in these experiments. The yields of polymeric ions of higher order usually increase rapidly in this range, but some of them, notably the yields of species with masses 83, 91, and 105, decrease linearly above 0.24 mm. Representative curves showing the characteristic source-pressure dependences of the normalized intensities

ties of various primary and higher order species appear in Fig. 2.

**2. Reaction Mechanisms.**—An effort has been made to bring some order to these complex "high pressure" mass spectra by assigning the more prominent polymeric or multiple-order ions to sequences of consecutive ion-molecule reactions, each beginning with one of the several primary precursors. Field<sup>5</sup> has attempted to do this by observing the increase in intensity of each secondary and tertiary species with increase in concentration of an additive gas in which electron impact gives rise mainly to one of the primary ions of  $C_2H_4$ . In contrast, our approach has been to compare the appearance potential of the polymeric ion with those of the primary species. Agreement of the values was taken as an indication that the polymeric ion was a transient in the chain of ion-molecule reactions starting with that particular primary. Our results are compared with those of Field in Table II. The values usually agree; but there are four discrepancies out of a total of eleven cases in which comparison may be made. It will be seen that where a difference occurs, our measurements indicate that the reactant is a primary species having fewer hydrogens than that represented by the findings of Field. It is of interest to note that the ion  $C_6H_5^+$  is found by us to have  $C_2H^+$  as its primary precursor rather than  $C_2H_3^+$  observed by the additive method (addition of  $C_2H_3Cl$ ). Field pointed out that the formation of this polymeric species by reaction of unexcited  $C_2H^+$  is energetically possible, whereas formation by  $C_2H_3^+$  in its ground state is not. Consequently, he was uncertain of the validity of the additive method in deducing the course of this particular ionic reaction.

TABLE II  
SETS OF TRANSIENT IONS INVOLVED IN CHAINS OF CONSECUTIVE ION-MOLECULE REACTIONS IN  $C_2H_4$

Primary ion	Intermediate ions	
	This work	Field (1961)
$C_2H_4$	$C_3H_5^+$ , $C_4H_8^+$ , $C_5H_9^+$	$C_3H_5^+$ , $C_4H_7^+$ , $C_4H_8^+$ , $C_5H_9^+$
$C_2H_3$	$C_2H_3^+$ , $C_4H_5^+$ , $C_4H_7^+$ , $C_5H_7^+$	$C_2H_3^+$ , $C_3H_5^+$ , $C_4H_5^+$
$C_2H_2$	$C_3H_3^+$ , $C_4H_3^+$	$C_3H_3^+$ , $C_4H_3^+$ , $C_4H_6^+$ , $C_5H_5^+$ , $C_6H_7^+$
$C_2H$	$C_3H_4^+$ , $C_5H_5^+$ , $C_5H_6^+$ , $C_5H_{11}^+$ , $C_6H_5^+$ , $C_6H_7^+$ , $C_6H_{11}^+$ , $C_7H_7^+$	

The relationships between primary ions and secondary ions, as revealed by our measurements of appearance potentials, are in good agreement with those observed by others<sup>5,9</sup> who used the same procedure but much lower gas pressures in their source chambers. Of the important secondary ions ( $C_2H_5^+$ ,  $C_3H_3^+$ ,  $C_3H_5^+$ ,  $C_4H_5^+$ , and  $C_4H_7^+$ ), there is disagreement only on the species  $C_4H_7^+$ . The appearance potential of the  $C_4H_5^+$  ion fell between those of  $C_2H_3^+$  and  $C_2H_2^+$  and it was difficult to decide which primary was the precursor. Consequently, it was listed with both in Table II.

**3. Determination of Reaction Cross Sections of Primary and Secondary Ions.**—Total reaction cross sections for the primary ( $\sigma_p^r$ ) and secondary ( $\sigma_s^r$ ) ions from  $C_2H_4$  with neutral ethylene molecules have been derived from treatment of the data on the dependence of ion intensity on the gas concentration according to the model previously described.<sup>4</sup> In this model the primary ions formed by electron impact followed by unimolecular dissociation of the parent ion are considered to form a "beam" which is attenu-

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

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

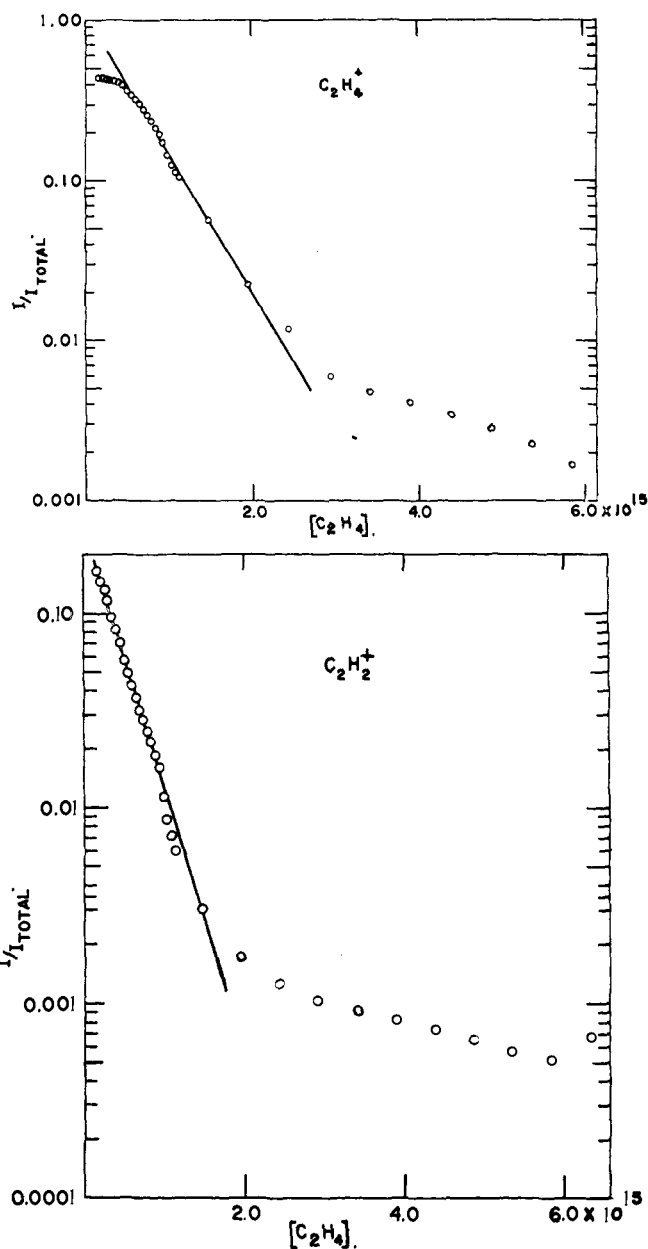


Fig. 3.—Semilogarithmic plots of normalized intensities of  $C_2H_4^+$  and  $C_2H_2^+$  ions vs.  $C_2H_4$  concentration (in molecules  $cm^{-3}$ ).

ated by ion-molecule reactions on traveling from the plane of origin to the exit slit of the source chamber of the mass spectrometer. The attenuation is expressed by the usual exponential equation

$$I_p = I_p^0 \exp(-\sigma_p^r [G] d) \quad (1)$$

where  $I_p$  (in ions per unit time per unit area) is the intensity of the particular primary ion at the source slit,  $I_p^0$  the intensity in the plane of electron ionization,  $\sigma_p^r$  the total reaction cross section (in  $cm^2$  molecule<sup>-1</sup>) of the primary species,  $[G]$  the concentration of ethylene (in molecules  $cm^{-3}$ ), and  $d$  the mean distance (in cm.) between plane of origin and exit slit. According to eq. 1, a graph of  $\log I_p$  vs.  $[G]$  should be a straight line from whose slope  $\sigma_p^r$  may be calculated. Since  $I_p^0$  and the ion-collection efficiency are functions of the gas pressure, it is necessary to normalize each intensity. This is done by dividing it by the total intensity of all ions at the indicated concentration of gas. Typical graphs, plotted as suggested by eq. 1, are shown in Fig. 3 for two primary ions from ethylene. The curve for  $C_2H_4^+$  is seen to be fairly

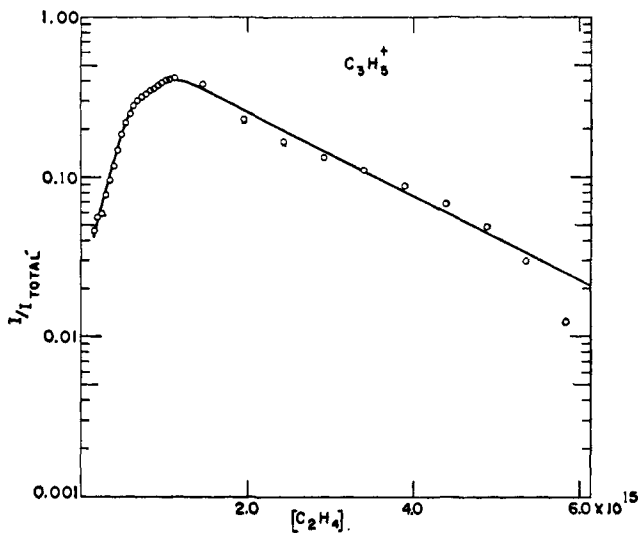


Fig. 4.—Semilogarithmic plot of normalized intensity of  $C_3H_5^+$  ion vs.  $C_2H_4$  concentration.

linear in the range of concentrations from  $0.2$ – $2.0 \times 10^{15}$  molecules  $cm^{-3}$ . The curvature found for this ion at very low concentration was also observed for  $C_2H^+$  and  $C^+$  but not in the plots of the other primary ions. Above the higher pressure, the two curves tend to flatten out. The latter behaviors may possibly be due to ion formation in very small amounts from dissociation of polymeric ions at the higher pressures. The cross sections listed in Table III are derived from the slopes of the initial linear portions of the curves. The values were reproducible within 20%.

The shape of the  $C_2H_4^+$  curve (Fig. 3) suggests that the species is behaving as a primary ion from electron impact and as a reactive secondary ion. Formation of this ion by charge exchange of  $C_2H_2^+$  with  $C_2H_4$  appears to be likely (see below). Since the  $C_2H_4^+$  intensity is increased by charge exchange at the same time that it is being attenuated by reaction, the cross section listed in Table III may be too low. However, the primary ion yield of  $C_2H_2^+$  in the mass spectrum of  $C_2H_4$  is only about one-half that of  $C_2H_4^+$ . In addition, the fraction of  $C_2H_2^+$  which charge exchanges is estimated to be about  $2/3$ , as indicated by comparison of the total reaction cross section of  $C_2H_2^+$  with the partial ones for the competitive ion-molecule reactions which form  $C_3H_3^+$  and  $C_4H_5^+$ . The latter reactivities were estimated from the initial slopes of the curves of the ratios  $I(C_3H_3^+)/I(C_2H_2^+)$  and  $I(C_4H_5^+)/I(C_2H_2^+)$  plotted as a function of ethylene concentration. Consequently, the contribution to  $C_2H_4^+$  by charge exchange is only one-third that formed directly by electron impact. Furthermore, charge exchange should compete less favorably with ion-molecule reactions as the concentration of gas increases, because the extent of acceleration of the ion between formation and collision with a gas molecule decreases. Since the cross section for an exoergic charge exchange is little affected by the velocity of the ion while ion-molecule reaction cross sections decrease with  $1/v$  to  $1/v^2$  of the ionic velocity, the charge exchange reaction yielding  $C_2H_4^+$  should be less important at the higher gas pressures. The foregoing considerations suggest that the total reaction cross section measured for  $C_2H_4^+$  by our method may be too low by no more than 20%.

The cross sections from source 2 are seen to be somewhat higher than the corresponding ones from source 1 but are still in reasonable agreement. But the reactivities we observed are considerably higher than those, listed in the same table, calculated from results

TABLE III  
TOTAL REACTION CROSS SECTIONS OF SEVERAL PRIMARY IONS  
FROM  $C_2H_4$  (REPELLER FIELD = 12 V./CM.)

$m/e$	Primary ion (singly charged)	$\sigma_p\tau$ , $10^{-16}$ $cm^2$ molecule $^{-1}$			Lampe, Field, and Franklin 1957
		Source 2	Source 1	Field 1961	
28	$C_2H_4^+$	62	45	13	45
27	$C_2H_3^+$	47	35	17	32
26	$C_2H_2^+$	93	65	18	34
25	$C_2H^+$	135			32
14	$CH_2^+$	85			
13	$CH^+$	92			

of Field.<sup>5</sup> The latter are summations of cross sections for specific, very prominent reactions of the given primary ion, which were determined by a different experimental procedure from that described above in this section. The measurements of Lampe, Field, and Franklin,<sup>5</sup> also listed in Table III, fall between ours and Field's. Melton and Rudolph<sup>6</sup> have published rate constants for some  $C_2H_4$  reactions, but they do not give either the mean transit times of their ions nor their mean lengths of trajectories. Consequently, it is not possible to convert their rate constants to cross sections for comparison with ours.

The expression relating the intensity of a secondary ion to the reaction cross sections, gas concentration, and mean travel distance is

$$I_s = \frac{I_p^0 \sigma_p}{\sigma_s \tau - \sigma_p} \{ \exp(-\sigma_p [G] d) - \exp(-\sigma_s \tau [G] d) \} \quad (2)$$

in which  $I_s$  is the intensity of the secondary species,  $\sigma_s \tau$  is the total reaction cross section of the secondary species, and  $\sigma_p$  is the partial cross section for reactions leading from the primary species to the secondary ion of interest. A graph of  $\log I_s$  as a function of ethylene concentration should rise at low  $[G]$ , but should fall off linearly at higher concentrations with a slope dependent on  $\sigma_s \tau$ , provided  $\sigma_s \tau < \sigma_p$ . The graph of the intensity of  $C_3H_5^+$  vs.  $[C_2H_4]$ , normalized as described above, is presented in Fig. 4. The slope of the approximately linear section of each such plot yields one of the cross sections compiled in Table IV. If  $\sigma_s \tau$

TABLE IV  
TOTAL REACTION CROSS SECTIONS OF SEVERAL SECONDARY IONS  
FROM  $C_2H_4$  (REPELLER VOLTAGE = 12 V./CM.)

$m/e$	Secondary ion (singly charged)	$\sigma_s \tau$ , $10^{-16}$ $cm^2$ molecule $^{-1}$	
		Source 1	Source 2
29	$C_2H_3^+$	26	28
39	$C_3H_3^+$	6	4
40	$C_3H_4^+$	15	19
41	$C_3H_5^+$	23	19
43	$C_3H_7^+$	17	18
51	$C_4H_2^+$	19	28
52	$C_4H_4^+$		22
53	$C_4H_5^+$	6	4
54	$C_4H_6^+$	5	5
55	$C_4H_7^+$	22	26

is greater than  $\sigma_p$ , the slope of the linear portion becomes a function of  $\sigma_p$ . As seen by comparison of the data in Table III, the cross sections assigned to secondary ions by this treatment of the data are clearly minimum values because in some cases they may represent the partial cross sections of primary ions giving the secondary ions of interest. Since the slope of each curve depends principally on the smaller cross section, a measured value indicating a cross section nearly equal to the partial cross section of the primary pre-

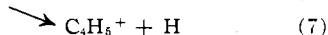
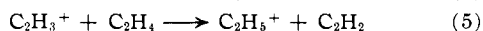
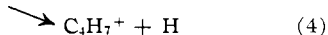
cursor actually shows that the cross section of the secondary ion must be greater than that of the primary. Where data may be compared, the agreement of the results from source 1 and source 2 is usually very good. It is seen that the reactivities of the secondary ions are also high, some reacting on first collision with an ethylene molecule.

### C. Discussion

According to Lampe,<sup>3</sup> when gaseous ethylene undergoes radiolysis, eleven gaseous organic products are observed, ranging from methane to *n*-hexane. Acetylene, hydrogen, *n*-butane, and ethane are the main products. Over the limited range of pressures studied by him, the *G*-values for product formation and for depletion of C<sub>2</sub>H<sub>4</sub> were invariant with pressure. At pressures below 20 cm. the yields of several products increase significantly.<sup>2a</sup> With the exceptions of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and polymer, the other major organic products are quenched by scavenging action of NO.<sup>10</sup> However, the gaseous products account for only about one-third of the ethylene which reacts, and therefore polymerization of C<sub>2</sub>H<sub>4</sub> to nonvolatile compounds is the dominant reaction.

Lampe<sup>3,11</sup> and others<sup>2a,b</sup> have already suggested that ion-molecule reactions are a possible key to understanding the mechanisms of radiolysis of ethylene. But, as these workers have pointed out, complete correlations of the results of ion-molecule reactions with those of radiolytic measurements have been unsuccessful. Yet the results of the mass spectrometric studies of ion-molecule reactions show that the reactions of not only the primary ions but also the secondary ions are very fast. There is also indication that higher order polymeric species are formed rather efficiently. Since the reactions between ions and molecules are much more rapid than some free-radical processes (for example, radical recombination and radical-molecule reactions requiring an activation energy), these ionic reactions must be considered as taking part in the stages of the mechanisms initiated by the radiation field and leading to the products observed. In the following discussion we will attempt a partial correlation based on the observations at the higher concentrations of C<sub>2</sub>H<sub>4</sub> in the source chamber of the mass spectrometer. Reactions initiated by excitation processes alone have been neglected.

Measurements on ion-molecule reactions in the mass spectrometer, both those performed at lower source pressures<sup>8,9</sup> than those described in this paper and those at the higher concentrations reported here and by others,<sup>5,6</sup> have shown that the primary ions produced by electron impact on C<sub>2</sub>H<sub>4</sub> react efficiently with the gas. The reactions of the primary ions which may be important for the understanding of the radiolysis of C<sub>2</sub>H<sub>4</sub> are



It is quite possible that, as a result of the ionization of ethylene by the radiation field and subsequent unimolecular dissociation of the parent ion, methane is formed by ionic reactions 3 and 6 followed by hydrogen abstraction by the excited CH<sub>3</sub> radical, *i.e.*, by the reaction

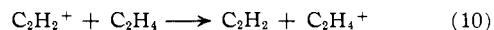


which may occur very rapidly and therefore not be affected by NO scavenger. If one accepts the values tabulated by Field and Franklin<sup>12</sup> for the heats of formation of the species taking part in reactions 3 and 6, 19 and 24 kcal./mole, respectively, are liberated as excitation energies in the two reactions. The activation energy for the hydrogen abstraction reaction 8 is 10.0 kcal./mole,<sup>13a</sup> which is somewhat greater than the 7.0 kcal./mole required for the competing reaction involving addition of the methyl radical to ethylene.<sup>13b</sup> On this basis, sufficient energy may not be available for reaction 8 because of division of the energy among the degrees of freedom of the ion and methyl radical. However, the errors in estimating heats of reaction are sufficiently great (probably of the order of 10–20 kcal./mole) that sufficient excitation may be available for the proposed reaction.

Intramolecular detachment of hydrogen has been shown to be the principal mode of formation of acetylene.<sup>2a,b</sup> Sauer and Dorfman<sup>2a</sup> suggest that this comes about by decomposition of an excited state of ethylene and/or by the proton transfer reaction



the latter mechanism having previously been proposed by Lampe.<sup>3</sup> But Field<sup>5</sup> and Čermák and Herman,<sup>14</sup> in a position diametrically opposite to that of Rudolph and Melton,<sup>15</sup> claim evidence that a mode of formation of C<sub>2</sub>H<sub>2</sub> is the charge-exchange reaction



Our results offer some evidence in support of Field and of Čermák. As observed from Fig. 3, the curve of the normalized intensity of C<sub>2</sub>H<sub>4</sub><sup>+</sup> turns downward with decreasing concentration at the lower end of the concentration range, but that of C<sub>2</sub>H<sub>2</sub><sup>+</sup> does not. Such a behavior would be expected if the plot were a superposition of a curve representing exponential attenuation of a primary ion and a curve showing the growth and decay of a secondary ion (*cf.* Fig. 4), which could be a C<sub>2</sub>H<sub>4</sub><sup>+</sup> formed *via* reaction 10. Another bit of evidence is the following data which suggests an apparent reaction competing with those of C<sub>2</sub>H<sub>2</sub><sup>+</sup> to form C<sub>3</sub>H<sub>3</sub><sup>+</sup> and C<sub>4</sub>H<sub>5</sub><sup>+</sup> (Table II). Above about 0.24 mm. pressure of C<sub>2</sub>H<sub>4</sub> in the source chamber, the normalized intensity curves of these secondary ions rise again after falling off over a large range below this pressure. This behavior is not exhibited by any of the other secondary ions. Possibly above 0.24 mm. the ion-molecule reactions of C<sub>2</sub>H<sub>2</sub><sup>+</sup> with C<sub>2</sub>H<sub>4</sub> compete more favorably with charge exchange because of slowing down of the ions by collision. Note further that the disagreement between our cross section for C<sub>2</sub>H<sub>2</sub><sup>+</sup> and that of Field, *et al.*,<sup>8</sup> is quite large although there is reasonable agreement for the other two major primary ions from ethylene (Table III). Our higher value would be expected if charge exchange contributed in large measure to the total reaction cross section. The procedure of Field, Franklin, and Lampe measures only reactivities in usual ion-molecule reactions (*i.e.*, not simple charge-transfer processes).

It is tempting to ascribe the behavior of C<sub>2</sub>H<sub>4</sub><sup>+</sup> in Fig. 3 to charge transfer from C<sub>2</sub>H<sub>2</sub><sup>+</sup> according to eq. 10. There is, however, one difficulty in this interpretation of the data. If this were the case, an

(12) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, Appendix and p. 129.

(13) (a) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 169 (1951); (b) L. Mandelcorn and E. W. R. Steacie, *Can. J. Chem.*, **32**, 79 (1954).

(14) V. Čermák and Z. Herman, *Collection Czech. Chem. Commun.*, **27** (2), 406 (1962).

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

(10) G. G. Meisels and T. Sworski, private communication.

(11) F. W. Lampe, "5th World Petroleum Congress Proceedings," New York, N. Y., June, 1959, Section X, pp. 109–119.

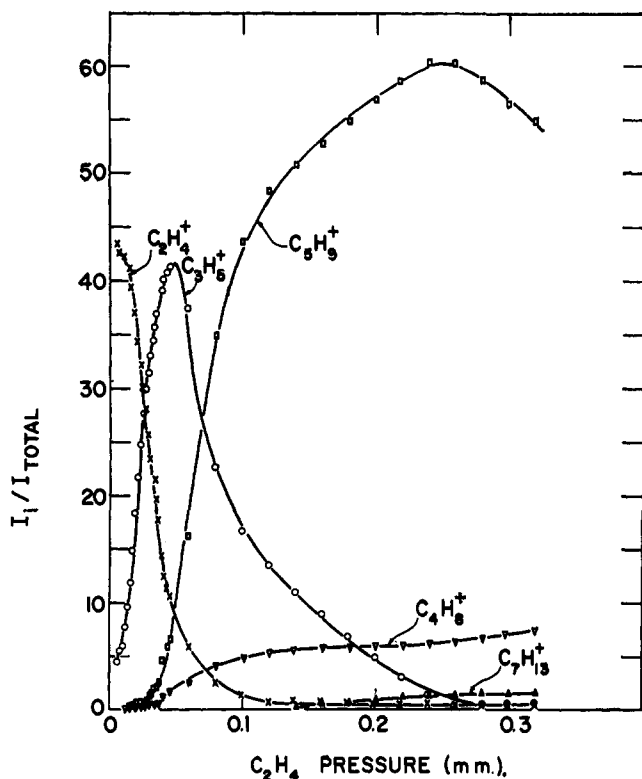


Fig. 5.—Behavior of normalized intensities of ionic species in the  $C_2H_4^+$  chain of consecutive ion-molecule reactions as a function of the ethylene pressure in the source.

abnormal break would be expected in the ionization-efficiency curve for  $C_2H_4^+$ , one which would indicate its formation by a secondary process involving  $C_2H_2^+$ . This was not found. The shapes of the curves for the  $C_2H_4^+$  species were similar to those for the other primary ions. On the other hand, the shape of the ionization-efficiency curve may not be very sensitive to such secondary processes. The intensity of an ionic species increases rapidly and linearly with the excess energy above the appearance potential. Thus, the abundance of  $C_2H_4^+$  from the primary ionizing act may completely obscure any  $C_2H_4^+$  arising from prior formation of  $C_2H_2^+$  (a process requiring an electron energy 3.0 e.v. higher than for  $C_2H_4^+$ ).

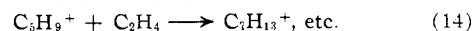
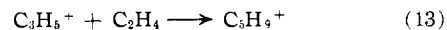
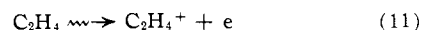
Our data and those of Field and of Cermak may be interpreted as indications that charge transfer is highly likely. They thus support the calculation of Dorfman and Sauer,<sup>16</sup> who assumed this charge exchange to find an interesting agreement between the ratio  $G(C_2H_2)/G(H_2)$  of 1.6, estimated from ion-molecule reactions, and the measured value of 1.8. The former number is obtained from reactions 9, 10, and  $H_2$  abstraction from  $C_2H_4^+$ . We have recalculated this ratio, using a more recent mass pattern for the primary ions from impact of electrons on ethylene,<sup>17</sup> and taking into account the unimolecular dissociation  $C_2H_4^+ \rightarrow C_2^+ + 2H_2$  in addition to the two,  $C_2H_4^+ \rightarrow C_2H_2^+ + H_2$  and  $C_2H_4^+ \rightarrow C_2H^+ + H_2 + H$ , considered by Dorfman and Sauer. With the fractional yield of each primary ion and the value of 3.88 ion pairs produced in ethylene per 100 e.v., we find  $G(H_2) = 1.10$ , and assuming eq. 9 and 10,  $G(C_2H_2) = 1.9$ . But, as shown above, only about two-thirds of the  $C_2H_2^+$  reacts by charge exchange, the remainder forming  $C_3H_3^+$  and  $C_4H_5^+$  by ion-molecule reactions.

Taking this into account,  $G(C_2H_2) = 1.6$ . The ratio is 1.5. This is to be compared with the more recent experimental determination<sup>2a</sup> of 2.0. In the absence of the charge-exchange reaction 10, the calculated  $G(C_2H_2)$  falls to 1.0 and the ratio  $G(C_2H_2)/G(H_2)$  amounts to only 0.9. But the agreement, if any, may be entirely fortuitous because the same ratio is obtained on photolysis of ethylene,<sup>18</sup> and it is not known how the energy of the radiation field is distributed among the various states of excitation and ionization.

The isotopic mixing observed by Sauer and Dorfman<sup>2a</sup> in the radiolysis of  $C_2H_4-C_2D_4$  mixtures may be accounted for plausibly by invoking ion-molecule reactions. The  $C_2H_2$  formed in the charge exchange of eq. 10 may be left in an excited state in which it may exchange hydrogens with a  $C_2H_4$  or  $C_2H_2$  molecule. The same may be true of the acetylene product of the proton transfer reaction 9. Such isotopic mixing of the acetylene product is not observed in direct photolysis<sup>18</sup> nor in mercury-photosensitized<sup>19</sup> decomposition of ethylene. In these radiation fields, of course, no ions should be formed. The ionic reactions also may explain the removal of isotopic mixing of hydrogens and deuteriums in the presence of nitric oxide.<sup>2a</sup> The quenching is accomplished without a decrease in the  $G$ -value for formation of acetylene. Possibly, deactivation of the excited  $C_2H_2$ , formed in the charge exchange and proton transfer reactions, by collision with NO is the mechanism by which the mixing is interrupted.

Since several products of higher molecular weight (*e.g.*, butane and hexane) are scavenged by NO, relatively long-lived free radicals should be intermediates in the mechanisms of their formation. These products can indeed be accounted for by the reactions of free radicals,<sup>20</sup> but the reactive radicals may be formed in ionic reactions. Thus  $CH_3$  and  $H$  may be formed as a result of ion-molecule reactions such as 3, 4, 6, and 7.

It was pointed out in the introduction to this paper that polymerization was by far the most important consequence of the radiolysis of ethylene. Wagner<sup>21</sup> has recently found that under the action of ionizing radiation solid  $C_2H_4$  at  $-196^\circ$  polymerizes to low-molecular-weight monoolefinic branched polymers. The fact that mixtures of  $C_2H_4$  and  $C_2D_4$  give compounds containing deuterium in multiples of four shows that the initiating species contains four hydrogen atoms. He suggests that the polymerization may be initiated by the  $C_2H_4^+$  molecule ion, propagated by ion-molecule condensation, and terminated by electron recombination. On the basis of our observations, we should like to propose a similar initiating and propagating mechanism for the low-pressure (0.1–10 mm.) gas-phase polymerization of ethylene, except that the "sticky" condensate in the first step breaks up and the propagation of the polymerization is by reaction of carbonium ions rather than molecule ions in the sequence



Evidence for these ionic reactions is furnished by the agreement of the appearance potentials (Table II) and the behaviors of the normalized intensities of the species  $C_2H_4^+$ ,  $C_3H_5^+$ ,  $C_5H_9^+$ , and  $C_7H_{13}^+$  with increasing concentration of ethylene (Fig. 5). Note that the intensity of  $C_2H_4^+$  decreases exponentially

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

(17) American Petroleum Institute Research Project 44, Catalogue of Mass Spectral Data (Carnegie Institute of Technology, 1953), Serial No. 65.

(18) M. C. Sauer, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).

(19) R. J. Cvetanović and A. B. Callear, *ibid.*, **23**, 1182 (1955).

(20) M. C. Sauer, Jr., private communication.

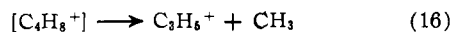
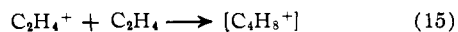
(21) C. D. Wagner, *J. Phys. Chem.*, **66**, 1158 (1962).

while that of  $C_3H_5^+$  increases by the same amount. The latter then decreases and  $C_5H_9^+$  increases. Finally, above 0.26 mm. the intensity of  $C_5H_9^+$  drops off, while that of  $C_7H_{13}^+$  is increasing. This behavior of the  $C_7H_{13}^+$  species, characteristic of a quaternary ion, suggests that it belongs in the  $C_2H_4^+$  chain of consecutive ion-molecule reactions and not in the  $C_2H_3^+$  sequence. There is almost a one-to-one relation between increase and decrease in abundances between adjacent pairs of ions among the first three in this sequence of consecutive ion-molecule reactions. Rudolph and Melton<sup>6</sup> have already suggested the persistent collision in eq. 13 as the mode of formation of  $C_5H_9^+$ . Such reactions have recently been observed in some alkyl halides<sup>22</sup> and in acrylonitrile and benzene.<sup>23</sup>

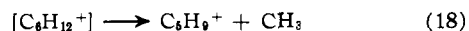
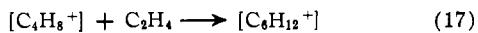
It is seen from Fig. 5 that the intensity of the tertiary species  $C_5H_9^+$  rises to a peak about 30% higher than the initial intensity of the  $C_2H_4^+$  ion, but that the total intensity of all ions in the sequence remains constant within about 20% over the entire pressure range. We believe the latter figure is due to the variation in ion collection efficiency of the mass spectrometer in this region of pressures, and it may not be unreasonably large. The fact that the  $\Sigma I_i/I_{total}$  is about 0.55 rather than 0.44, the initial fractional yield of the  $C_2H_4^+$  precursor, is explained by the formation of  $C_2H_4^+$  by charge transfer between  $C_2H_2^+$  and ethylene. If two-thirds of the 24% initial percentage of  $C_2H_2^+$  in the mass pattern of ethylene undergoes this reaction (see above), it would be equivalent to increasing the initial fractional yield of  $C_2H_4^+$  from 0.44 to 0.60. The latter number agrees very well with the summed fractional intensity of about 0.55 cited above.

The polymeric species  $C_4H_8^+$  behaves (Fig. 5) as if it were a tertiary rather than a secondary ion; its intensity dependence resembles that of  $C_5H_9^+$  rather than of  $C_3H_5^+$ . Therefore, we believe the  $C_4H_8^+$  species is not the product of a usual persistent collision between a  $C_2H_4^+$  and  $C_2H_4$ , but possibly is a reaction complex stabilized by collision with an ethylene molecule. Field<sup>5</sup> has also concluded that  $C_4H_8^+$  is a tertiary ion.

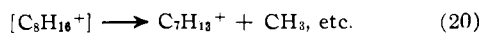
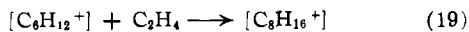
In contrast to the sequence of reactions 12-14 stated above, the model of Lampe, Franklin, and Field<sup>5,24</sup> proposes that this ionic condensation would proceed through reactions of undissociated intermediate reaction complexes. Thus



or



or



(22) R. F. Pottie and W. H. Hamill, *J. Phys. Chem.*, **63**, 877 (1959).

(23) A. Henglein, *Z. Naturforsch.*, **17a**, 44 (1962).

(24) F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," Vol. 1, G. Porter, Ed., Pergamon Press, London, 1961, p. 69.

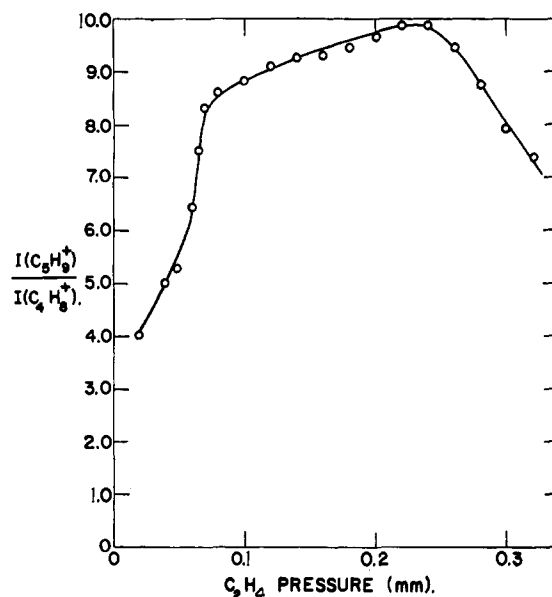
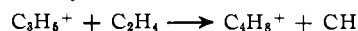


Fig. 6.—Variation of the intensity ratio  $I(C_5H_9^+)/I(C_4H_8^+)$  with pressure of ethylene in the source chamber.

Comparison of the two proposed sequences indicates that the validity of one over the other depends on whether the reaction complex  $[C_4H_8^+]$  dissociates into  $C_3H_5^+ + CH_3$  before it reacts with another ethylene molecule. Convincing evidence for either of the alternate paths is, however, lacking at present. Theoretical calculations of the lifetime of the complex against unimolecular dissociation, using the standard kinetic expression, gave values which varied over several orders of magnitude, depending on the activation energy and number of effective oscillators. The estimated range of lifetimes bracketed the lifetime of the complex against reaction with a  $C_2H_4$  molecule.

Experimentally, however, the  $C_4H_8^+$  species is observed as a tertiary species (Fig. 5 and ref. 5). Indeed, the shapes and positions of the intensity curves for  $C_4H_8^+$  and  $C_5H_9^+$  suggest that the two are the products of a common precursor. Since it is doubtful that  $C_4H_8^+$  is formed by reaction of the secondary ion  $C_3H_5^+$



because this reaction is endoergic by 76 kcal./mole, the only alternative course is by a stabilizing collision of the intermediate complex  $C_4H_8^+$  with a  $C_2H_4$  molecule. By this reasoning, then, the common precursor to  $C_4H_8^+$  and  $C_5H_9^+$  is the  $C_6H_{12}^+$  transient. But if this is so, the ratio of the intensity of  $C_5H_9^+$  to that of  $C_4H_8^+$  should be independent of pressure, provided neither species is formed by some other reaction. In Fig. 6 one sees that the ratio varies by a factor of 2.5. Consequently, it is not clear if a collision of  $C_4H_8^+$  with  $C_2H_4$  results in a reaction other than that of removing excitation energy from the ion.

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