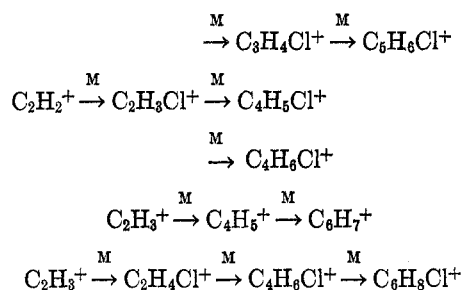


## Ionic Reactions in Unsaturated Compounds. IV. Vinyl Chloride

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Mass spectrometric studies of ion-molecule reactions in vinyl chloride have resulted in the identification of three ionic polymerization sequences



In most cases the indicated condensation reactions proceed with elimination of HCl or C<sub>2</sub>H<sub>2</sub>. Isotopic studies show that the principal reaction of low velocity parent ions is charge transfer, the rate constant for this process being some 30 times larger than the summation of rates for other ion-molecule reactions. It is further observed that vinyl chloride parent ions produced directly by electron impact react to give a distribution of condensation products which is substantially different from that which results from the reactions of parent ions formed by charge transfer. This is interpreted in terms of differences in the internal energy of the collision complexes formed by the two types of reactant ions. An examination of the dependence of the product distribution from this reaction on both internal and translational energy of the reactants shows that the former is the more important factor in this system. The results of the present investigation are compared with data on ionic processes in vinyl chloride obtained by other techniques.

## Introduction

The radiolysis of vinyl chloride in the gaseous phase, using an  $\alpha$ -particle source, was investigated some time ago by Mund and coworkers.<sup>4-8</sup> These studies indicated that the "ionic" yield of monomer consumption is strongly dependent upon the experimental conditions for radiolysis, but they provided little information concerning the actual nature of the ionic reactions which occur in the vinyl chloride system. It seems likely, however, that degradation products, such as hydrogen and methane, which are produced by radiolysis, may result from ionic condensation reactions.<sup>9</sup>

Recently, ion-molecule reactions in vinyl chloride have been examined by the use of a new technique which employs ion cyclotron resonance spectroscopy.<sup>10</sup> Condensation reactions were indeed observed for this compound but most of these were found to involve elimination of HCl as the neutral species. Some interesting isotope effects were also reported in this study. In view of the considerable number of uncertainties which are still associated with the use of a cyclotron resonance instrument for the investigation of ion-molecule reactions, it seemed appropriate to undertake a study of vinyl chloride using the more conventional mass spectrometric techniques which we

have employed in earlier studies in this laboratory.<sup>11-13</sup> Because of the somewhat larger polarizability of the halocarbon and its permanent dipole moment, the reactivity of the vinyl chloride might be expected to be significantly greater than that of the simple hydrocarbons previously studied. For these several reasons the detailed mass spectrometric study of vinyl chloride described in this paper was therefore initiated.

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(4) W. Mund and J. A. Herman, *Bull. Acad. Roy. Belg.*, **37**, 333 (1951).

(5) W. Mund, J. A. Herman, and P. Huyskens, *ibid.*, **37**, 696 (1951).

(6) W. Mund, J. A. Herman, and G. Verfaillie, *ibid.*, **35**, 656 (1949).

(7) W. Mund, M. Van Meerssche, and J. Momigny, *Bull. Soc. Chim. Belges*, **62**, 109 (1953).

(8) W. Mund, M. Van Meerssche, and J. Momigny, *ibid.*, **62**, 645 (1953).

(9) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience Publishers, Inc., New York, N. Y., 1962.

(10) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

(11) J. H. Futrell and T. O. Tiernan, *J. Phys. Chem.*, **72**, 158 (1968).

(12) T. O. Tiernan and J. H. Futrell, *ibid.*, **72**, 3080 (1968).

(13) F. P. Abramson and J. H. Futrell, *ibid.*, **72**, 1994 (1968).

## Experimental Section

The experimental approach applied in this study is similar to that used in the previous investigations in this series.<sup>11-13</sup> High-pressure single-source experiments were accomplished with a modified time-of-flight mass spectrometer, which has recently been described in some detail,<sup>14</sup> in order to search for sequential reaction processes and to evaluate kinetic parameters. In this instrument the ion path length from the collimated electron beam to the source exit aperture is 0.28 cm. For all the experiments reported here, the electric field strength in the source was maintained at 10.6 V/cm by applying an appropriate repeller potential to the source backing grid. The source temperature was held at 250° for all these studies and the ionizing voltage was set at 100 V. In order to minimize space charge effects, the electron current was adjusted to approximately  $1 \times 10^{-8}$  A with no gas in the source prior to a particular experiment. Gas was then introduced into the ion source from a reservoir by means of a motor-driven gas leak which is controlled by a Granville-Phillips Series 213 automatic pressure controller. The input signal for the controller was an MKS Baratron Model 77H1 pressure transducer, connected by a static pressure tap directly to the ion source chamber. The latter was set to the desired ion source pressure and the pressure is held constant within about 1% of the selected value throughout an experiment. After introducing the gas and allowing a short period for stabilization of the source, the mass range of interest was scanned and recorded. Data reduction requires a correction for mass discrimination, as already described,<sup>14</sup> because of the technique used to achieve space-focus for time-of-flight mass analysis.

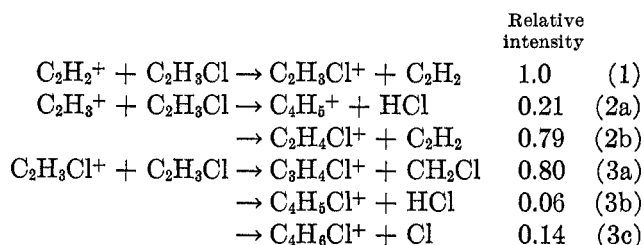
Studies of elementary ion-molecule reactions of individually selected ions were carried out using the ARI tandem mass spectrometer, which has also been described previously.<sup>15</sup> For the experiments reported in this paper, the kinetic energy of the mass-analyzed impacting ion beam was maintained at 0–0.4 eV except where otherwise indicated. Pulse-counting techniques were used for measuring product ion intensities.

Vinyl chloride used in these experiments was obtained from the Matheson Co. and was purified by conventional vacuum distillation. Gas chromatographic analysis indicated only trace impurities.

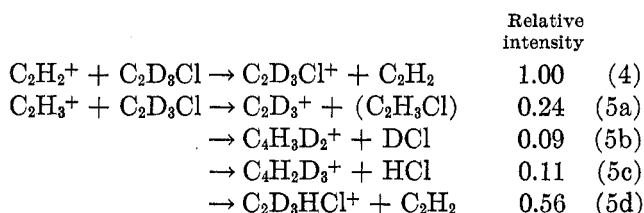
## Results and Discussion

The low-pressure mass spectrum of vinyl chloride is comparatively simple, consisting of only four ions of appreciable intensity which have the relative abundances:  $C_2H_2^+$ , 32.3%;  $C_2H_3^+$ , 100%;  $C_2H_3^{35}Cl^+$ , 84.5%;  $C_2H_3^{37}Cl^+$ , 26.6%. Therefore, it is the ion-molecule reactions of these four principal primary ions which will be of significance for the vinyl chloride system. The reaction of each of these ions with the parent molecule was examined in the tandem mass spectrometer at a

reaction chamber pressure of 5  $\mu$ . The observed ionic products and their relative intensities in each case are indicated by the series of reactions 1–3c.



In order to investigate the details of reactions 1 and 2, the acetylene and vinyl ions were treated with vinyl chloride- $d_3$ .

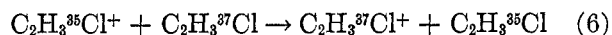


Reaction 4 shows that the charge-transfer reaction of acetylene ion with vinyl chloride- $d_3$  does not involve an intimately bonded intermediate complex since no hydrogen is incorporated in the charge-transfer product. It can probably best be interpreted as an electron-transfer reaction. However, reactions 5a–5d show that in addition to the  $C_4X_5^+$  product and  $C_2X_4Cl^+$  products observed in reactions 2a and 2b, about 24% of the total reaction of vinyl ions yields a  $C_2D_3^+$  product. The corresponding product from reaction 2 is not detected since it would be obscured by the primary signal. This reaction could proceed either by a  $Cl^-$  transfer from the vinyl chloride molecule to the vinyl ion, by proton transfer from the ion to the neutral species, followed by dissociation of the excited protonated ion to yield the products indicated, or by dissociative charge transfer. Both the latter reactions are highly endothermic for ground-state ions and tentatively may be ruled out. Reaction 5d shows that simple proton transfer is the most important reaction in which the vinyl ion participates, while reactions 5b and 5c suggest that the  $C_4X_5^+$  product is formed from an intermediate complex which eliminates HCl and DCl with about equal probability. An identical distribution for the  $C_4X_5^+$  products was obtained when  $C_2D_3^+$  reacted with  $C_2H_3Cl$ . This suggests that the products in both of these cases result from decomposition of  $(C_4D_3H_3Cl^+)^*$  complexes which are very similar in structure and internal energy, and a normal isotope effect in the decomposition of the complex is responsible for the fact that  $C_4H_3D_2^+$  constitutes 44% of the total  $C_4X_5^+$  product.

(14) J. H. Futrell, T. O. Tiernan, F. P. Abramson, and C. D. Miller *Rev. Sci. Instr.*, **39**, 340 (1968).

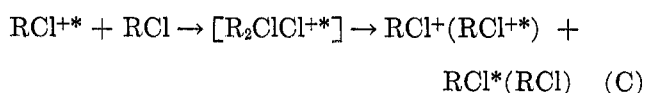
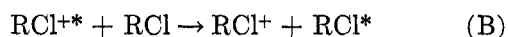
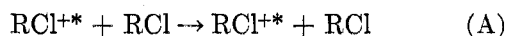
(15) J. H. Futrell and C. D. Miller, *Rev. Sci. Instr.*, **37**, 1521 (1966).

In addition to reactions 3a-3c of the parent vinyl chloride ion, reaction 6, the charge-transfer reaction, was also observed.



The corresponding reaction with  $\text{C}_2\text{H}_3^{35}\text{Cl}$  neutrals cannot be observed in the tandem spectrometer, but if it is assumed to occur with the same cross section as reaction 6, then simply on the basis of the relative abundances of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  neutrals in the vinyl chloride reactant, this reaction should be more intense by a factor of 3 than reaction 6. This would mean that the total charge-transfer reaction of  $\text{C}_2\text{H}_3\text{Cl}^+$  ions with vinyl chloride has a cross section which is larger by a factor of 30 than the other ion-molecule reactions of this ion. Reactions of  $\text{C}_2\text{D}_3\text{Cl}^+$  with  $\text{C}_2\text{H}_3\text{Cl}$  are reported in Table VI and will be discussed in a later section.

Further information on reactions 3a-3c can be obtained from a study of the isotopic chlorine distribution in the product ion resulting from impact of  $^{35}\text{Cl}$  or  $^{37}\text{Cl}$  reactant ions. Since the minor chlorine isotope is of substantial natural abundance and since the reactant ion is mass selected in the tandem instrument, it is possible to investigate the source of the chlorine atom which ultimately appears in the product ion. Three limiting cases for a given reaction may be considered. The product ions may retain the chlorine isotope of the reactant ions (case A), the chlorine isotope of the reactant neutrals (case B), or may consist of ions containing chlorines from both reactants, the isotopes being distributed



in a purely random fashion (case C). The latter distribution is anticipated if the ion-molecule reaction under consideration involved the formation of an intermediate collision complex which is sufficiently long-lived to permit scrambling of the chlorine isotopes. The calculated distribution of isotopic chlorine in the product ions which would be expected for each of these three cases is shown for both  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  reactant ions

**Table I:** Calculated Distribution of Isotopic Chlorine Products for Reactions of Ions with Vinyl Chloride

Isotope in reactant ion	Isotopic distribution of product ions					
	Mechanism					
	A		B		C	
	$^{35}\text{Cl}$	$^{37}\text{Cl}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$
$^{35}\text{Cl}$	1.0	0	0.75	0.25	0.88	0.12
$^{37}\text{Cl}$	0	1.0	0.75	0.25	0.38	0.62

**Table II:** Observed Distribution of Isotopic Chlorines in Selected Product Ions for Reactions of Various Ions with Vinyl Chloride

Reactant ion	Product ions, %					
	$\text{C}_2\text{H}_4\text{Cl}^+$		$\text{C}_4\text{H}_5\text{Cl}^+$		$\text{C}_4\text{H}_7\text{Cl}^+$	
	$^{35}\text{Cl}$	$^{37}\text{Cl}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$	$^{35}\text{Cl}$	$^{37}\text{Cl}$
$\text{C}_2\text{H}_3^{35}\text{Cl}^+$	86.6	13.4	82.8	17.2	87.6	12.4
$\text{C}_2\text{H}_3^{37}\text{Cl}^+$	38.8	61.2	...	...	39.8	60.2
$\text{C}_2\text{H}_4^{35}\text{Cl}^+$	NR	NR	NR	NR	87.4	12.6
$\text{C}_2\text{H}_4^{37}\text{Cl}^+$	NR	NR	NR	NR	37.9	62.1

in Table I. The experimentally observed distributions are shown in Table II for reactions of both isotopic species of two different ions.

A comparison of the calculated and experimental data of Tables I and II clearly indicates a randomized chlorine distribution in the product ions and strongly suggests that the reactions of  $\text{C}_2\text{H}_3\text{Cl}^+$  and  $\text{C}_2\text{H}_4\text{Cl}^+$  proceed through  $[\text{C}_4\text{H}_6\text{Cl}_2^{+*}]$  and  $[\text{C}_4\text{H}_7\text{Cl}_2^{+*}]$  intermediates, respectively. Although observing the chlorine distribution alone could lead to incorrect conclusions about chlorine randomization,<sup>16</sup> the deuterated vinyl chloride results shown in Table III support this mechanism.

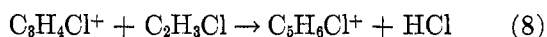
**Table III:** Total Reaction Cross Sections for Ions with Vinyl Chloride

Ion	Cross section, Å <sup>2</sup>
$\text{C}_2\text{H}_2^+$	102
$\text{C}_2\text{H}_3^+$	71
$\text{C}_2\text{H}_3\text{Cl}^+$	37
$\text{C}_2\text{H}_4\text{Cl}^+$	38

Higher order ion-molecule reactions in vinyl chloride are also of interest. Except in unusually favorable cases, pressure limitations on the tandem spectrometer make it impossible to obtain secondary ionic species from the first stage in sufficient abundance to use as reactant ions. Consequently, sequential reactions were investigated by using source molecules which produce by primary fragmentation ions of the same empirical formula as the secondary, tertiary, etc., ions formed in vinyl chloride. For the ions of interest here,  $\text{C}_2\text{H}_4\text{Cl}^+$  was obtained from 1,2-dichloropropane,  $\text{C}_3\text{H}_4\text{Cl}^+$  from 1,2,3-trichloropropane, and  $\text{C}_4\text{H}_5^+$  from 1,2-butadiene.

(16) In a study of ion-molecule reactions in methyl and ethyl chlorides in our laboratory, chlorine randomization was suggested by the chlorine isotope distribution observed in the protonated alkyl chloride product. When the corresponding reactions were studied using the deuterated parent ions, it was clear that a combination of hydrogen transfer from the neutral molecule and deuterium transfer from the reacting ion was actually occurring. It appears that the protonated alkyl chloride ion is not formed through a randomized intermediate complex but rather that it is produced by simple hydrogen atom and proton-transfer reactions.

The products from these ions are shown in reactions 7a through 9.



Again, the product distributions shown in Table II suggest that reaction 7 goes through an intermediate complex in which chlorine randomization occurs. Similar results were observed from the product from reaction 8. Reaction 7b is apparently a simple proton transfer from the protonated vinyl chloride to a vinyl chloride molecule. Reaction 9 could only be observed at high collision chamber pressures ( $40 \mu$ ) and apparently requires collision with a third body for it to occur. A note of caution should be injected in attributing reactions 7 through 9 to the actual reactions of secondary ions in the vinyl chloride system. There may well be differences in both internal energy and structure between secondary ions derived from ion-molecule reactions and those derived from primary fragmentation.

*Experiments at Elevated Pressures.* Vinyl chloride was also studied at pressures up to  $200 \mu$  in a modified time-of-flight mass spectrometer. Figures 1 and 2 illustrate the observed pressure dependences of the intensities of the various ions in the reaction sequence. Figure 1 shows the variation with pressure of vinyl ions and those products which were identified in the tandem

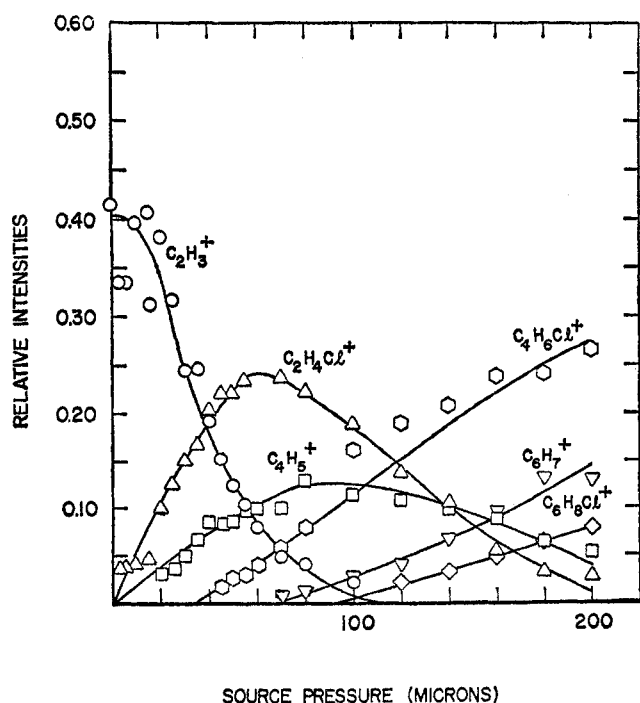


Figure 1. Pressure dependence of vinyl ion and the ionic products ultimately derived from it.

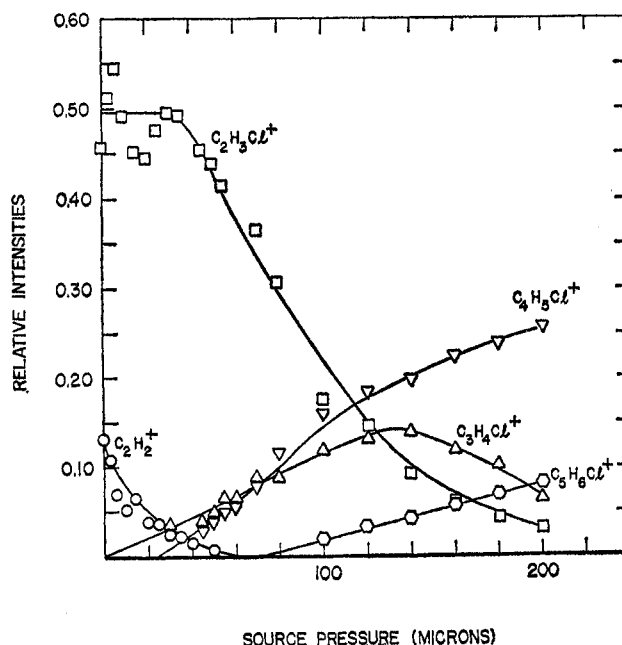


Figure 2. Pressure dependence of vinyl chloride and acetylene ions and products ultimately derived from their reactions.

experiments as having the vinyl ion as a precursor. The observed pressure dependence of relative ion intensities is in accord with the reaction sequence deduced. Similarly, Figure 2 shows the pressure variation of the parent ion and products ultimately derived from its reactions. The apparent "induction" period before parent ion is noted is attributed to the production of vinyl chloride molecular ions *via* the charge exchange reaction of acetylene ion with vinyl chloride (reaction 1). Once acetylene ion has been removed by reaction, the relative intensity of parent ion declines monotonically with pressure.

From semilogarithmic plots of the pressure data, total reaction cross sections were derived for the three major primary ions and for the protonated parent ion (Figure 3). These cross-section data are listed in Table IV. It is apparent that the cross section for the charge-transfer reaction of acetylene ion with vinyl chloride is quite large, and it is to be expected that a substantial fraction of the parent ion will be produced by this path as well as by direct electron impact. Also since the charge transfer of the parent ion with vinyl chloride was indicated by the tandem mass spectrometer study to be some 30 times as important as the other ion-molecule reactions, it is probable that most of the parent ions produced from electron impact undergo charge transfer before a change-of-identity reaction occurs. Further evidence supporting this assertion will be presented subsequently. The lower cross sections measured for the other three ions listed in Table III are understandable in view of the results of the isotopic experiments already cited. The latter experiments showed that all three of these ions have prominent back-reaction channels. In normal experi-

**Table IV:** Reactions of  $C_2H_3Cl^+$ ,  $C_2D_3Cl^+$ ,  $C_2H_2^+$ , and  $C_2D_2^+$  with  $C_2H_3Cl$  at Various Collision Chamber Pressures in the Tandem Mass Spectrometer at a Temperature of 25°

Impacting ion	Pressure, $\mu$	$C_2H_3Cl^+$	$C_3H_4Cl^+$	$C_3H_3DCl^+$	$C_3H_2D_2Cl^+$	$C_3HD_3Cl^+$	$C_4H_5Cl^+$	$C_4H_4Cl^+$	$C_4H_3D_2Cl^+$	$C_4H_2D_3Cl^+$	$C_4H_3D_3Cl^+$
$C_2H_3Cl^+$	5	48,600	1130	0	0	0	194	290	0	0	0
	25	100,000	4540	0	0	0	2430	1610	0	0	0
$C_2D_3Cl^+$	5	39,000	0	291	209	348	26	24	48	82	179
	25	100,000	1880	855	530	1137	1610	1030	267	482	749
$C_2H_2^+$	5	46,500	0	0	0	0	0	0	0	0	0
	25	100,000	1640	0	0	0	1070	700	0	0	0
$C_2D_2^+$	5	50,000	0	0	0	0	0	0	0	0	0
	25	100,000	1520	0	0	0	844	535	0	0	0

ments these reaction modes are not detected since they yield ionic products of the same mass as the reactant. Thus it is not surprising that the observed cross sections for the ions in question are somewhat lower than typically expected.

Additional information regarding the mechanism of the ionic processes involved can be obtained from the high-pressure data by the determination of the orders of formation of the individual ionic species. Since the intensity of a product ion of order,  $n$ , is proportional to

the  $n$ th power of pressure, the reaction order for a particular ion will be given by the slope of a plot of the logarithm of ion intensity as a function of  $\log$  (vinyl chloride) pressure. Figures 4 and 5 show such plots for various product ions. In these figures the true order of formation of a particular ion will actually be one order higher than that indicated directly by the slope because relative ion intensities (normalized to the total ionization summation) have been used instead of absolute values.

In these figures solid straight lines have been drawn with the appropriate slopes of 1, 2, or 3, for comparison with actual experimental points represented by the various symbols. It is observed that the data fit these lines quite accurately in most cases. Hence we conclude that the ions  $C_4H_5^+$  and  $C_2H_4Cl^+$  are second-order products, the ions  $C_3H_4Cl^+$ ,  $C_4H_5Cl^+$ , and  $C_5H_6Cl^+$  are

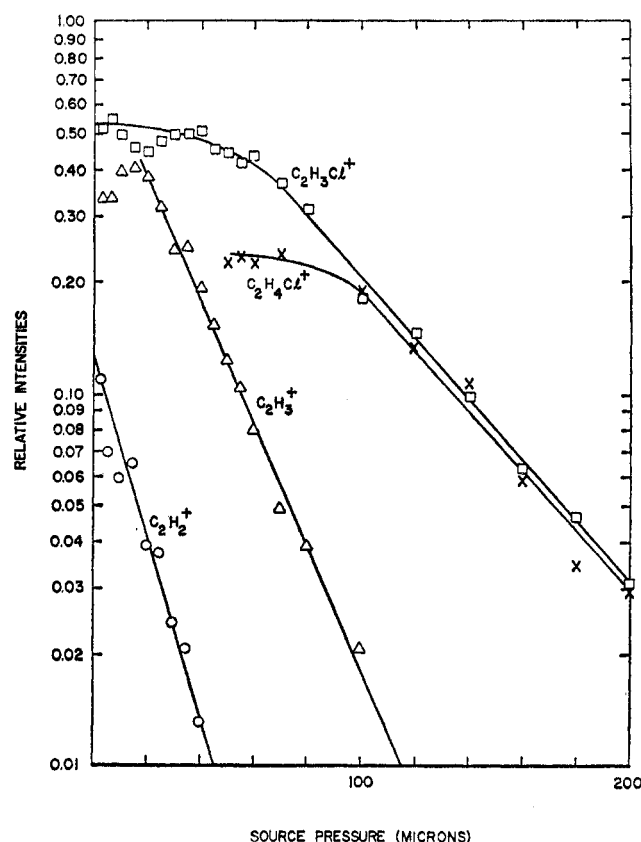


Figure 3. Semilogarithmic plots of relative intensities vs. source pressure for the primary ions and protonated vinyl chloride.

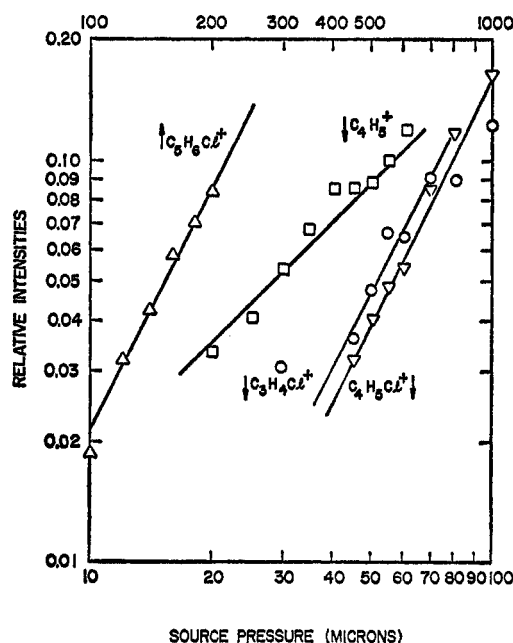


Figure 4. Logarithmic plots of relative intensities vs. source pressure for ion products in vinyl chloride.

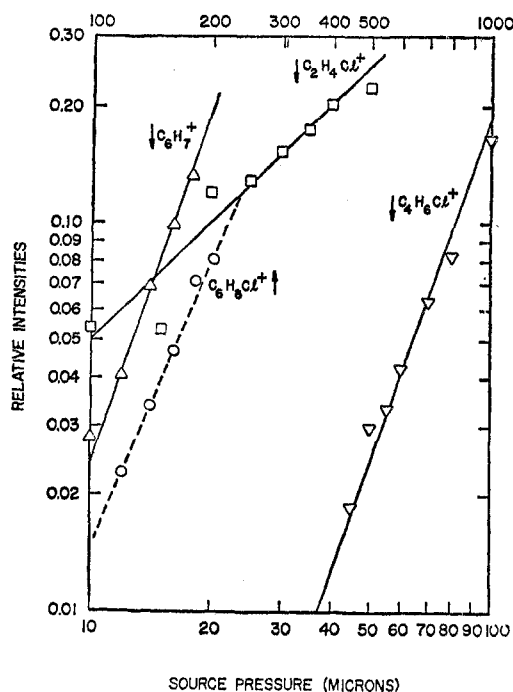


Figure 5. Logarithmic plots of relative intensities vs. source pressure for ion products in vinyl chloride.

third order, and the  $C_6H_7^+$  and  $C_4H_6Cl^+$  products are fourth-order ions. The dashed line drawn through the experimental points for the  $C_6H_5Cl^+$  ion is of a non-integral slope suggesting that this ion is of mixed order (third and fourth).

With the exception of the  $C_4H_5Cl^+$  and  $C_4H_6Cl^+$ , the orders determined for these products are in agreement with those predicted by the reaction sequence established by the tandem mass spectrometric results. However, the  $C_4H_5Cl^+$  and  $C_4H_6Cl^+$  products are one reaction order higher than expected. Here the tandem spectrometer sequence indicates that  $C_4H_5Cl^+$  is formed by reaction 3b while  $C_4H_6Cl^+$  must result mainly from reaction 7a. The tandem data and the single source data are also in disagreement as to the relative amounts of the  $C_3H_4Cl^+$  and  $C_4H_5Cl^+$  products. The ratio of products  $C_3H_4Cl^+/C_4H_5Cl^+ = 0.80/0.06$  was found in the tandem experiments while the ratio is  $0.06/0.05$  at  $30\ \mu$  in the single-stage instrument,

**Reactivity of the Parent Ion.** It is clear that there are significant discrepancies between the single source and the tandem mass spectrometric results for higher order ionic products in vinyl chloride. Since the over-all reaction sequence appears consistent in both types of experiments, the question of reactant identity does not appear to be the problem. However, there are two notable differences in the properties of primary reactant ions which are formed in these two instruments. In the first place, with the repeller potential employed, the reactant ions in the time-of-flight source have kinetic energies ranging from 0 to 3 eV, while ions in the primary beam of the tandem spectrometer have both a very low

kinetic energy and only a small energy spread (0–0.3 eV ion energy) for the experiments under consideration. Secondly, the pressure in the time-of-flight ion source is greater than that in the collision chamber of the tandem, typically by a factor of 10 or more. This means that reactant ions in the former case can undergo multiple collisions whereas a collision chamber pressure of  $5\ \mu$  for the tandem ensures single-collision conditions. Consequently, there may be substantial differences in the reactivity of the same ion under the two types of experimental conditions. Moreover, the isotopic studies carried out with the tandem spectrometer show that the production of parent ions by charge transfer from both the acetylene ion and the molecule ion is an important process. The parent ions produced by charge transfer may be expected to differ considerably in internal energy content from those produced directly by electron impact. It is therefore likely that the two types of parent ions react quite differently with regard to the production of higher order products.

In order to explore this possibility, the product distributions from impact of  $C_2H_2^+$ ,  $C_2D_2^+$ ,  $C_2H_3Cl^+$ , and  $C_2D_3Cl^+$  ions on vinyl chloride were determined in the tandem mass spectrometer as a function of collision chamber pressure. At low collision chamber pressure, ( $5\ \mu$ ), further reactions of the parent ions produced by charge transfer are negligible. Further, for the experiments with impacting  $C_2D_3Cl^+$  ions, the isotopically mixed products,  $C_3X_4Cl^+$ ,  $C_4X_5Cl^+$ , and  $C_4X_6^+$  ( $X = H$  or  $D$ ), are a measure of secondary ions derived directly from the impacting parent ions. At a collision chamber pressure of  $25\ \mu$ , however, the  $C_2H_3Cl^+$  ions produced by charge transfer suffer subsequent collisions with neutral vinyl chloride molecules. These ions can therefore react further and contribute to higher order products at this pressure. Since the products derived from the charge-transfer sequence contain no deuterium, the reaction products from the two types of precursor  $C_2H_3Cl^+$  ions can be distinguished by such experiments.

Table IV shows the results of impacting these several ions on  $C_2H_3Cl$  at various collision chamber pressures. When the impacting ion is  $C_2H_3Cl^+$ , no distinction can be made between the condensation products formed from  $C_2H_3Cl^+$  produced by primary ionization and charge exchange. However, a comparison of the 5- and 25- $\mu$  product distributions is quite instructive. The ratio of products  $C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$  of 0.70:0.12:0.18 at  $5\ \mu$  is altered to 0.53:0.28:0.19 at  $25\ \mu$ . As outlined above, interpretation of the vinyl chloride ion reactions is further clarified by impacting  $C_2D_3Cl^+$  on  $C_2H_3Cl$ , since the products formed from the impacting ion contain deuterium and those derived from reaction of the charge-exchange product contain no deuterium. At  $5\ \mu$  the data of Table IV show that no  $C_3H_4Cl^+$  and only trace quantities of  $C_4H_5Cl^+$  and  $C_4H_6Cl^+$  are produced. At  $25\ \mu$  increased amounts of  $C_2H_3Cl^+$  produced by charge exchange and the sub-

**Table V:** Ratios of Higher Order Products Produced by Various Reactant Ions as a Function of Collision Chamber Pressure at a Temperature of 25°

Impacting ion	C <sub>2</sub> H <sub>3</sub> Cl pressure, $\mu$	C <sub>3</sub> X <sub>4</sub> Cl <sub>total</sub> <sup>+</sup> :C <sub>4</sub> X <sub>5</sub> Cl <sub>total</sub> <sup>+</sup> : C <sub>4</sub> X <sub>6</sub> Cl <sub>total</sub> <sup>+</sup>	C <sub>3</sub> H <sub>4</sub> Cl <sup>+</sup> :C <sub>4</sub> H <sub>5</sub> Cl <sup>+</sup> :C <sub>4</sub> H <sub>6</sub> Cl <sup>+</sup>	C <sub>3</sub> D <sub>n+1</sub> H <sub>3-n</sub> Cl <sup>+</sup> :C <sub>4</sub> D <sub>n+2</sub> H <sub>3-n</sub> Cl <sup>+</sup> : C <sub>4</sub> D <sub>3</sub> H <sub>3</sub> Cl <sup>+</sup>
C <sub>2</sub> H <sub>3</sub> Cl <sup>+</sup>	5	0.70:0.12:0.18	0.70:0.12:0.18	...
	25	0.53:0.28:0.19	0.53:0.28:0.19	...
C <sub>2</sub> D <sub>3</sub> Cl <sup>+</sup>	5	0.70:0.13:0.17	...	0.73:0.11:0.15
	25	0.52:0.28:0.21	0.42:0.36:0.23	0.63:0.19:0.19
C <sub>2</sub> H <sub>2</sub> <sup>+</sup>	5	...	...	...
	25	0.48:0.31:0.20	0.48:0.31:0.20	...
C <sub>2</sub> D <sub>2</sub> <sup>+</sup>	5	...	...	...
	25	0.52:0.29:0.18	0.52:0.29:0.18	...

sequent reaction products C<sub>3</sub>H<sub>4</sub>Cl<sup>+</sup>, C<sub>4</sub>H<sub>5</sub>Cl<sup>+</sup>, and C<sub>4</sub>H<sub>6</sub>Cl<sup>+</sup> are observed.

Two significant facts are apparent from the data. First, if the amount of totally hydrogenated products is compared with the mixed products, it appears that the charge-transfer molecular ion is somewhat more reactive than the molecular ion beam which is produced directly by electron impact. Also, since there is a change in product distribution observed for reaction of C<sub>2</sub>H<sub>3</sub>Cl<sup>+</sup> with vinyl chloride at elevated pressure, it is interesting to note the variation of the C<sub>3</sub> and C<sub>4</sub> product distribution as a function of chamber pressure. Table V shows the relative distributions for the three higher order products for the reaction sequence initiated by the various ions. The first column represents the ratio of the total amounts of these products formed. The second column shows only the ratio of these products which contain no deuterium—that is, the distribution resulting from the charge-transfer ion except for the case of C<sub>2</sub>H<sub>3</sub>Cl<sup>+</sup> reactant. The third column gives the ratio for the mixed products from reaction of C<sub>2</sub>D<sub>3</sub>Cl<sup>+</sup> with C<sub>2</sub>H<sub>3</sub>Cl and therefore shows the product distribution for the primary ion produced directly by electron impact. It can be seen that the total C<sub>3</sub> and C<sub>4</sub> product distributions observed for the C<sub>2</sub>H<sub>3</sub>Cl<sup>+</sup> and C<sub>2</sub>D<sub>3</sub>Cl<sup>+</sup> reactions with vinyl chloride (shown in column 1) are identical. However, a comparison of the product distribution derived from the parent ion formed by charge exchange with that produced by primary parent ion shows that the two are distinctly different. Moreover, there is a slight change in the product distribution formed directly from the C<sub>2</sub>D<sub>3</sub>Cl<sup>+</sup> primary ion with increasing pressure, as shown in column 3. This is possibly due to collisional degradation of the energy of either the C<sub>4</sub>X<sub>6</sub>Cl<sub>2</sub><sup>+</sup> complex or of the primary ion itself prior to reaction. The latter is possible since a substantial number of "nonreactive" collisions occur in this system.

The product distributions for the vinyl chloride parent ion produced by charge exchange from C<sub>2</sub>H<sub>2</sub><sup>+</sup>

and C<sub>2</sub>D<sub>2</sub><sup>+</sup> are also reported in Table V. Since the intensity of the acetylene ion from vinyl chloride is rather small, the reactions reported are for acetylene ions derived from acetylene and acetylene-*d*<sub>2</sub>. In one experiment C<sub>2</sub>D<sub>2</sub><sup>+</sup> from vinyl chloride-*d*<sub>3</sub> was impacted on vinyl chloride at 25  $\mu$  and the observed distribution of products was identical with that reported in Table V within experimental error. The small differences in the product distributions resulting from the two different acetylene ions and from the C<sub>2</sub>D<sub>3</sub>Cl<sup>+</sup> ion at 25  $\mu$  which are shown in column 2 are probably indicative of the reproducibility of these measurements.

The extreme sensitivity of the product distribution to the internal energy of the reaction complex prompted several additional experiments. In one series, the distribution of the products derived solely from the charge-transfer ion was studied as a function of collision chamber temperature. Table VI shows these results for charge-transfer parent ions produced from C<sub>2</sub>D<sub>3</sub>Cl<sup>+</sup>. By normalizing all the product distributions to the same charge-exchange intensity, the relative rates of reaction to form each product can be compared. A considerably larger fraction of the total reaction leads to condensation products at the lower temperatures than at the higher. Further, the relative yields show that there is an increase in the extent of fragmentation of the complex at higher temperatures; that is, there is an increase in C<sub>3</sub>H<sub>4</sub>Cl<sup>+</sup> at the expense of C<sub>4</sub>H<sub>5</sub>Cl<sup>+</sup>. Somewhat surprisingly, the C<sub>4</sub>H<sub>6</sub>Cl<sup>+</sup> relative intensity is a comparatively constant fraction of the condensation products over the entire temperature range, suggesting that it may be formed through a different complex.

A similar but less pronounced temperature effect is seen in Table VII which shows the effect of collision chamber temperature upon the product distribution from reaction of the parent vinyl chloride ion produced directly by electron impact. Again, at higher temperatures, the C<sub>3</sub> product is more important than in the room temperature reaction, although the C<sub>3</sub>H<sub>4</sub>Cl<sup>+</sup> fragment already constitutes a very large fraction of the

**Table VI:** Effect of Collision Chamber Temperature on the Higher Order Product Distribution and on the Relative Rate for Reaction of  $C_2H_3Cl^+$  Produced by Charge Transfer

Collision chamber temp, °C	$C_2H_3Cl^+$	$C_3H_4Cl^+$	$C_4H_5Cl^+$	$C_4H_6Cl^+$	Relative yields $C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$
200	100,000	557	184	213	0.58:0.19:0.22
160	100,000	878	398	406	0.52:0.24:0.24
130	100,000	995	482	436	0.52:0.25:0.23
100	100,000	1330	690	500	0.53:0.27:0.20
90	100,000	1200	712	610	0.48:0.28:0.24
25	100,000	1780	1540	930	0.42:0.36:0.21

**Table VII:** Effect of Collision Chamber Temperature on Higher Order Product Distribution from Reaction of  $C_2H_3Cl^+$  Produced Directly by Electron Impact

Collision chamber temp, °C	Relative yields $C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$
185	0.81:0.06:0.13
135	0.79:0.06:0.15
110	0.78:0.06:0.15
25	0.75:0.08:0.17

total products even at room temperature. Thus it appears that for this system the internal energy of the reacting ion is a major factor in determining the fragmentation channels of the reaction complex. An examination of the data in Table V further suggests that the parent molecule ion produced by electron impact must have considerably more internal excitation than the parent molecule ion formed by charge transfer.

In another series of experiments, the effect of reactant ion translational energy on the relative product distribution was examined. The reaction of the parent ion produced by electron impact was investigated over a rather narrow energy range. It was not possible to study the reaction at higher energies owing to the rapid decrease in reaction cross section with consequent reduction in product ion signal as the energy was raised. Table VIII shows that decreasing the primary ion energy by 0.2 eV results in a slight change in the  $C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$  distribution from 0.72:0.10:0.18 to 0.65:0.16:0.18. Essentially the same effect was observed for the distribution produced by secondary parent ions. Table IX shows the reactivity

**Table VIII:** Effect of Translational Energy of the  $C_2H_3Cl^+$  Reactant on the Product Distribution when  $C_2H_3Cl^+$  Is Produced by Electron Impact. Collision Chamber at 25°

Corr ion energy, eV	$C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$
0.50	0.72:0.10:0.18
0.40	0.70:0.12:0.18
0.30	0.65:0.16:0.18

and the product distribution for these as a function of primary ion energy. From the latter table it can be seen that there is an over-all decrease in reactivity of about 50% when the translational energy increases from 0.3 to 1.05 eV. The relative product distribution also changes in the direction of increased fragmentation to  $C_3H_4Cl^+$ . From 1.05 to 9.05 eV, there is effectively no change in the relative rates of reaction or in the product distribution. Thus it appears that while a small amount of the reactant ion translational energy is converted to internal energy of the complex, there is a limit to the efficiency of this conversion. These observations are consistent with the interpretation of a dual mechanism for charge transfer, one portion of this reaction resulting from a long-range electron jump process largely independent of relative velocity, and the other an orbiting complex component which is significant only at low relative velocity. On the whole, the reaction is relatively independent of reactant ion velocity and certainly this parameter is less significant than internal energy of the reactants for the case under consideration.

In view of the sensitivity of the parent ion reaction with vinyl chloride to internal energy of the reactants, it seemed appropriate to search for an effect of ionizing electron energy on the higher order product distribution. It was expected that this might provide evidence for the participation of excited states of the reactant  $C_2H_3Cl^+$  ions analogous to that obtained in a previous study of the acetylene system.<sup>17</sup> Accordingly, ionization efficiency curves for both primary ions and product ions in vinyl chloride were determined in a single-source instrument, using a C.E.C. 21-103C mass spectrometer at elevated pressures. Figure 6 presents these curves for the three most important primary ions in vinyl chloride along with that of  $Ar^+$  which was used as a reference ion. Taking a value of 15.76 eV for the appearance potential of  $Ar^+$ , the following ionization potential and appearance potentials were calculated.

$$IP(C_2H_3Cl^+) = 9.7 \pm 0.3 \text{ eV}$$

$$AP(C_2H_3^+) = 12.8 \pm 0.3 \text{ eV}$$

$$AP(C_2H_2^+) = 13.8 \pm 0.3 \text{ eV}$$

(17) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 35 (1945).



**Table IX:** Effect of Translational Energy of the  $C_2H_3Cl^+$  Reactant on the Higher Order Product Distribution when  $C_2H_3Cl^+$  Is Produced by Charge Transfer. Collision Chamber at 25°

Corr ion energy, eV	$C_2H_3Cl^+$	$C_3H_4Cl^+$	$C_4H_5Cl^+$	$C_4H_6Cl^+$	$C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+$
0.30	100,000	2220	1850	1200	0.42:0.35:0.20
0.55	100,000	1570	1040	722	0.47:0.31:0.22
1.05	100,000	1180	806	459	0.48:0.33:0.19
1.55	100,000	1110	727	451	0.49:0.32:0.20
2.05	100,000	1050	700	448	0.48:0.32:0.20
3.05	100,000	1100	625	471	0.50:0.28:0.21
4.05	100,000	1090	711	506	0.47:0.31:0.22
6.05	100,000	1100	823	561	0.44:0.33:0.23
9.05	100,000	1110	749	528	0.47:0.31:0.22

These values can be compared with previously reported observations of  $IP(C_2H_3Cl^+) = 10.0^{17}$  and  $AP(C_2H_3^+) = 12.8^{18}$ . Since the appearance potentials of the primary ions are quite widely separated, possible contributions to the higher order products can be readily assessed. Figure 7 shows the  $C_3H_4Cl^+$ ,  $C_4H_5Cl^+$ , and  $C_4H_6Cl^+$  product ion intensities along with the  $C_2H_3Cl^+$  and  $C_2H_2^+$  primary ion intensities as functions of elec-

tron energy. The top three curves are displaced to simplify the figure. The parent ion was identified as the source of the  $C_3$  and  $C_4$  products in the tandem spectrometer and, indeed, the onset of these products corresponds to the appearance potential of the  $C_2H_3Cl^+$  ion. However, the product ion curves do not track the parent ion ionization efficiency curve. Instead the product curves exhibit much sharper initial slopes than that of the parent ion. Further, although the primary ion intensity doubles between about 12.0 and 17.0 V, on the uncorrected electron energy scale, there is no additional production of the secondary products. At about 17.0 V there is a striking increase in the  $C_3$  and  $C_4$  product intensities which corresponds closely to the appearance potential of  $C_2H_2^+$  ion. This demonstrates clearly the occurrence of reaction 1 when  $C_2H_2^+$  ion is formed by primary fragmentation of vinyl chloride and once again establishes that there are two types of reactant parent ions which contribute to the higher order products.

In Figure 8, ionization efficiency curves for the primary ions are again shown along with those for  $C_4H_5^+$  and  $m/e$  63. As already noted, the tandem mass spectrometric studies show that  $C_4H_5^+$  and  $C_2H_4Cl^+$  are formed by reactions of the  $C_2H_3^+$  ion. In agreement with this, the  $C_4H_5^+$  product is observed to have the same appearance potential as the  $C_2H_3^+$  primary. On the other hand,  $m/e$  63 has a much less pronounced onset than does the  $C_4H_5^+$  product. This may be explained by the fact that at energies below the appearance potential of  $C_2H_3^+$ , the  $m/e$  63 product consists of  $^{13}C^{12}CH_3Cl^+$  rather than the protonated molecule ion.

It is appropriate to compare our results on ion-molecule reactions in vinyl chloride with the observations for this system from recent experiments conducted by Harrison.<sup>19</sup> The latter investigator has detected both second- and third-order components in the products from reaction of parent ion. He has determined the second-order product distribution to be in the ratio  $C_3H_4Cl^+ : C_4H_5Cl^+ : C_4H_6Cl^+ = 0.68:0.16:0.16$  at

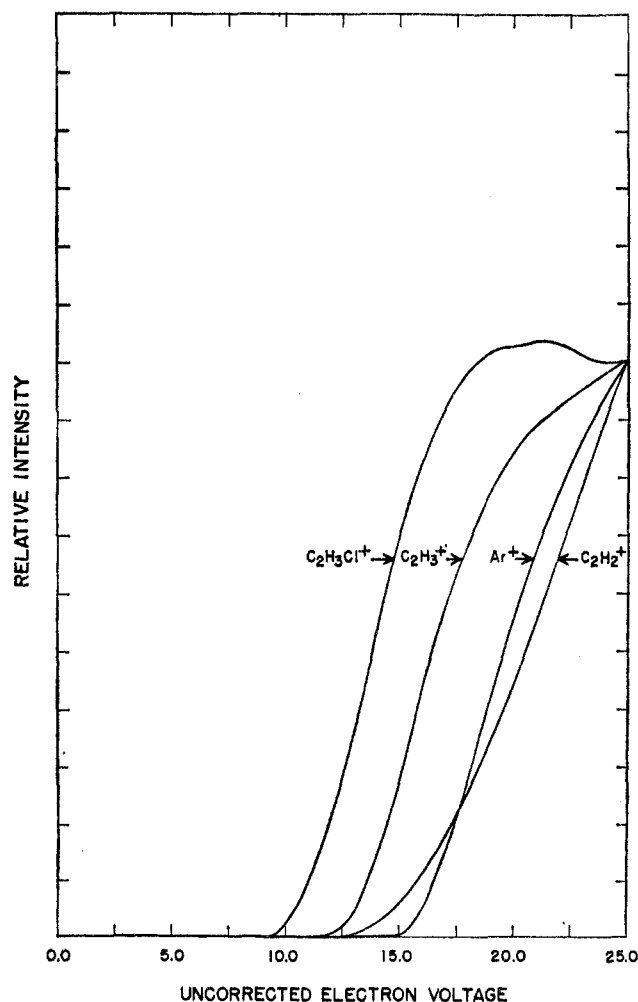


Figure 6. Appearance potential curves for the primary fragment ions of vinyl chloride.

(18) F. H. Field, *J. Chem. Phys.*, **21**, 1506 (1953).

(19) A. G. Harrison, private communication.

**Table X:** Ratio of  $C_2H_3Cl^+ : C_2H_5Cl^+ : C_4H_5Cl^+$  Product Distribution from Reactions of Parent Ions with Vinyl Chloride as Observed by Different Experimental Techniques

Source of $C_2H_3Cl^+$ reactant	Primary ionization	Charge transfer from $C_2D_3Cl^+$	Charge transfer from $C_2H_2^+$	High-pressure mass spectrometry (60 $\mu$ )
Product distribution from present work	0.80:0.06:0.14	0.42:0.36:0.23	0.48:0.31:0.20	0.40:0.34:0.26
Second-order product distribution from ref 19 (Harrison)	0.70:0.15:0.15			
Third-order product distribution from ref 19 (Harrison)		0.36:0.49:0.15		
Ion cyclotron resonance product distribution from ref 24 (Beauchamp)		0.31:0.58:0.11		

15 eV ionizing electron energy. This can be compared with the corresponding product distribution 0.70:0.12:0.18 observed in the present study for the reaction of parent ion with vinyl chloride at 25° and 5- $\mu$  collision chamber pressure in the tandem spectrometer. Harrison found the third-order product distribution to be 0.37:0.48:0.15, which again compares favorably with our distribution produced by charge-transfer parent ions of 0.42:0.36:0.23. These results are summarized in Table X.

Since Harrison's study involved only single-source experiments, he was unable to detect the charge-transfer

reaction of the parent ion directly. He has, however, made two significant observations which point to the occurrence of such a process. First, he has noted that the second-order rate constant for reaction of parent ions with vinyl chloride is lower by a factor of 100 than those typically observed for such bimolecular ion-molecule reactions. This would certainly be the case if charge transfer, which Harrison cannot take into account in his rate measurements, were the dominant mode of reaction for this ion. Moreover from our data in Table IV for the reaction of  $C_2D_3Cl^+$  ions with vinyl

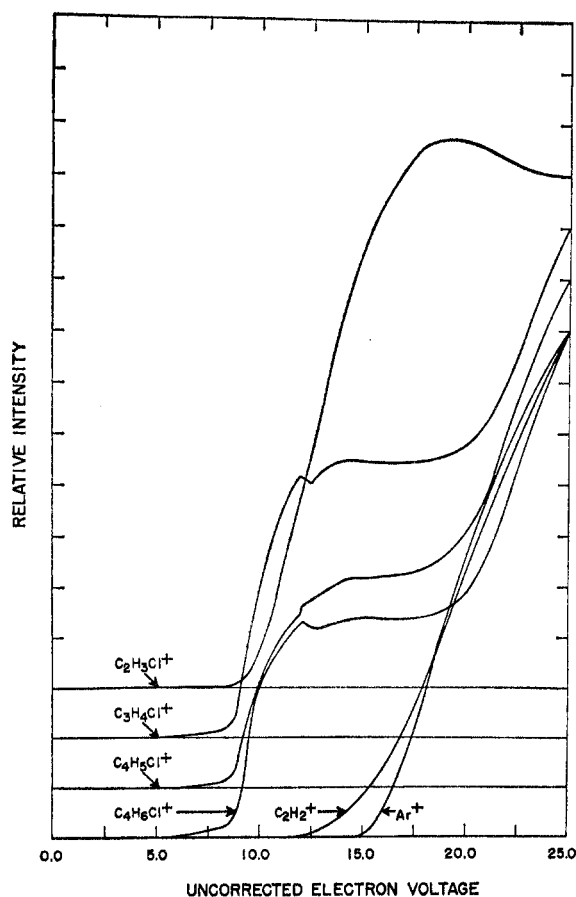


Figure 7. Appearance potential curves for the  $C_2H_3Cl^+$  and  $C_2H_5^+$  primary ions and for the  $C_3$  and  $C_4$  ionic secondary products.

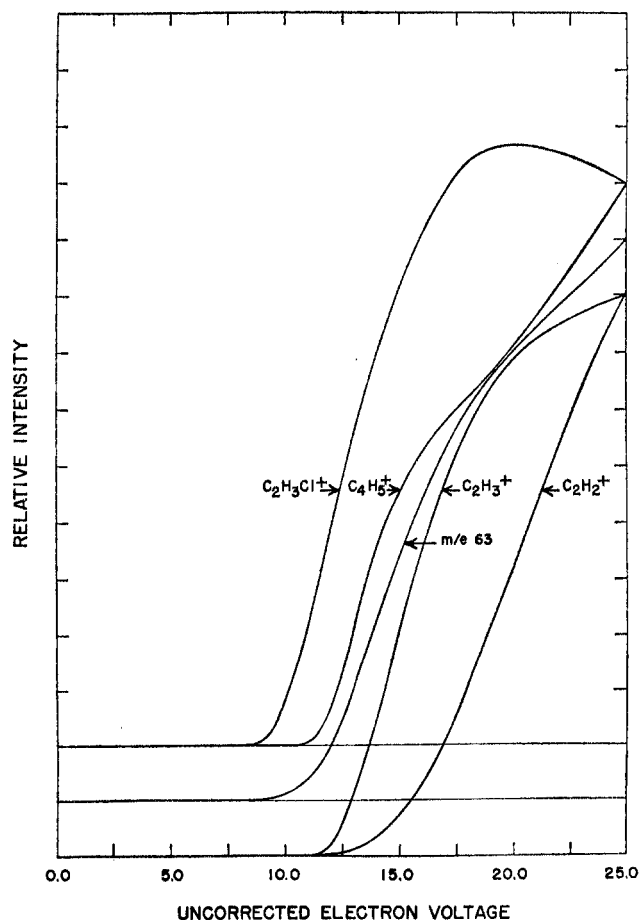


Figure 8. Appearance potential curves for the primary ions in vinyl chloride and the  $C_4H_5^+$  and  $m/e$  63 secondary products.

chloride, it can be seen that approximately equal amounts of condensation products are derived from the impacting ion and from the parent ion produced by charge transfer. It can be deduced from this that the rate constant for production of condensation products by the parent ion formed by charge transfer is about 100 times that for the primary parent ion since the intensity of the impacting ion beam is about  $10^2$  that of the charge-transfer product. Harrison's second observation which supports the charge-transfer sequence is his finding that at elevated source pressures, the withdrawal times for  $C_2H_3Cl^+$  ions become very long. This suggests that these ions have been retarded in their passage out of the source, which is readily accounted for as resulting from the predominant charge-transfer reactions.

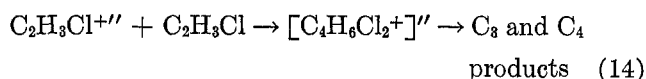
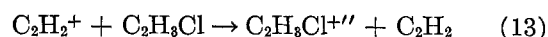
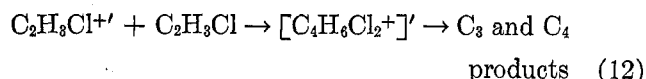
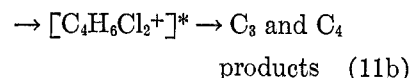
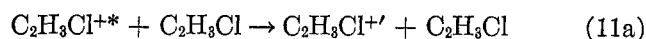
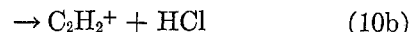
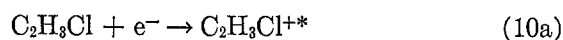
*Comparison of Ion Cyclotron Resonance Spectroscopy with Conventional Mass Spectrometric Techniques.* In a recent study of ionic reactions in vinyl chloride, Beauchamp, Anders, and Baldeschwieler<sup>10</sup> deduced the various ion-molecule reaction products using ion cyclotron resonance (icr) spectroscopy. In general their qualitative data are in good agreement with data obtained by conventional mass spectrometric techniques. Notable exceptions are the reported observation of  $C_6H_5^+$  and  $C_7H_7^+$  using icr while these ions were not detected in the present study. However, icr spectroscopy appears to be very sensitive to residual impurities in the system so that the  $m/e$  65 and 91 may be due to impurities. Beauchamp, *et al.*, also observed chlorine randomization in reactions 3a-3c, 7a, and 8, as we have discussed in an earlier section of this paper. However, in view of the complicated reaction sequence which our study has revealed, the significance of the latter observations is somewhat questionable. Higher reaction sequences were observed by icr spectroscopy using the double-resonance technique. Again these sequences are in general agreement with those which we observe using the combined tandem and high-pressure mass spectrometric techniques. However, the detailed behavior of the parent vinyl chloride ion which was observed in the present study and also to some degree in the single source study by Harrison<sup>19</sup> could not be elaborated in the icr study. Moreover, the data of Beauchamp, *et al.*, give no indication of the overwhelming predominance of charge transfer as the reaction mode for the parent vinyl chloride ion although this reaction was explicitly considered.

It is interesting to compare the relative distributions of secondary products from the parent ion reaction in vinyl chloride as determined by several different methods. Table X shows results reported by Beauchamp<sup>20</sup> using icr, along with the data obtained by Harrison in single-source measurements (to which we have already referred), and the relative yields observed in the ARL tandem mass spectrometer. The column headings give the conditions under which the vinyl

chloride parent ion was produced in our experiments. As noted above, Harrison's second-order product distribution has been included under the results for reaction of vinyl chloride parent ion produced directly by primary ionization, while his third-order product distribution is included under the distribution produced by reaction of parent vinyl chloride ion from charge transfer. It is somewhat more difficult to assign the icr data of Beauchamp since he reported neither isotopic studies nor measurements of reaction order. The best quantitative comparison, however, is obtained if the latter distribution is considered to result from the charge-transfer parent ion reactant. This implies that in the icr experiment essentially all of the reactant parent ions are produced by charge transfer, or the complex produced by the primary parent ions is degraded in energy to the extent that it decomposes in the same fashion as the complex formed by the secondary parent ions. As we have already mentioned, the product distributions from the two types of reactants appear to approach the same values with increasing numbers of collisions. The agreement between the distributions shown in Table X under the column labeled, "charge transfer from  $C_2D_3Cl^+$ ," is quite remarkable in view of the demonstrated sensitivity of the reaction to such parameters as temperature, translational energy, and excitation energy of the impacting ion, since these obviously vary rather widely in the several experiments considered. As we have seen, however, the product distribution resulting from secondary parent ions is much less affected by these parameters than is the primary parent distribution. Again, this suggests that charge transfer is much more important for the vinyl chloride system in the cyclotron resonance experiment than has been previously realized.

## Summary

The totality of the data obtained for vinyl chloride in the present study is best explained by the following reaction sequence for formation of the higher order condensation products.



From the appearance potential curves reported in

(20) J. L. Beauchamp, Doctoral Dissertation, Harvard University, 1968.

Figure 7, it can be deduced that the parent ion formed by electron impact in reaction 11a has in excess of 2.0 eV internal energy, probably in the form of vibrational energy. As already shown (reaction 6), charge transfer is more probable for this ion by a factor of 30 than an ion-molecule reaction resulting in a change of identity. Thus only a small fraction of the total reaction of this ion leads to the higher mass condensation products. Probably, in this case, any intermediate complex formed by an intimate collision is sufficiently excited that it fragments almost entirely to the original reactants. The parent ion produced by charge transfer in reaction 12a, however, is expected to differ considerably in internal energy from that produced by direct electron impact and it is apparent that ion-molecule reactions leading to condensation products (by way of an intermediate complex having less excitation energy) are much more favorable for this ion. It seems clear from the data presented in Tables IV and V that the collision complexes produced in reactions 11b, 12, and 14 must have different amounts of internal energy. It also appears that with increasing pressure, the complexes formed in all these processes fragment similarly, since the product distributions all approach the same ratios at higher pressures. This presumably indicates that, at some pressure, all the complexes are reduced to

the same level of internal excitation by collisional deactivation. Our results clearly establish that excitation energy of the reactants can dramatically affect the internal energy of the reaction complex. For the vinyl chloride system, however, the translational energy of the reacting ion appears to be much less important than internal energy.

There remains to be explained the fourth-order dependence observed for the  $C_4H_6Cl^+$  ion in the high-pressure study. This is possibly explained on the basis of an extra reaction step which would logically involve reaction 7b. That is, two protonation sequences would precede the production of  $C_4H_6Cl^+$ , and this is perhaps understandable if the  $C_2H_4Cl^+$  precursor is highly excited. This additional reaction step would further isolate the  $C_4H_6Cl^+$  yield with respect to the influence of the various reaction parameters discussed in this work, and, indeed, the relative yield of this product seems to be very little affected by these factors.

*Acknowledgment.* The authors express their gratitude to Professor A. G. Harrison for access to his data prior to publication and also for stimulating discussions of ion-molecule reaction problems. They are also indebted to Dr. J. L. Beauchamp for permission to cite unpublished results from his doctoral thesis.

## Chemical Effects of Charge-Transfer Absorption. I. The Photoinduced Chain Reaction between Thallium(I) and Thallium(III)

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Ultraviolet irradiation of  $^{204}Tl$ -labeled thallium(I)-thallium(III) solutions induces rapid exchange with quantum yields ranging from 2 to 30 or higher. Initiation is due to charge-transfer absorption in  $Tl_{aq}^{3+}$  and  $TlOH^{2+}$  producing a thallium(II) chain carrier. Rate constants for the propagation reactions of thallium(II) with thallium(I) and thallium(III) are derived. Chain termination is largely quadratic disproportionation of thallium(II), but at low light intensities, a linear termination reaction is more important. The relevance of these observations to the thermal mechanism for thallium(I)-thallium(III) exchange is discussed.

### Introduction

The high-intensity absorption band of metal complexes, which normally occurs in the 2500–3200-Å region, is often described as a charge-transfer band.<sup>1–3</sup> An alternative molecular orbital description<sup>4</sup> is one of electronic excitation from a bonding orbital to a non-bonding or antibonding orbital. Whereas the charge-

transfer microsymmetry is linear suggesting that the excitation involves only a single ligand and the central

- (1) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).
- (2) J. N. Murrell, *Quart. Rev. (London)*, **15**, 191 (1961).
- (3) F. S. Dainton, Special Publication No. 1, The Chemical Society, London, 1954, p 18.
- (4) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Reading, Mass., 1962.