

I. PROTON AFFINITIES OF ATMOSPHERIC GASES

II. REACTIONS OF THE ALKYL HALIDES

A thesis presented

by

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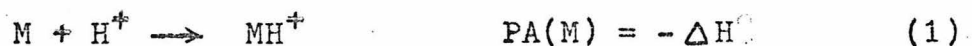
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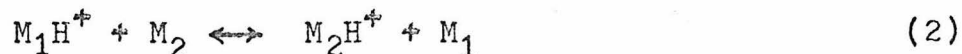
I. PROTON AFFINITIES OF ATMOSPHERIC GASES

A. Introduction

Proton transfer reactions are one of the simplest, yet most important, classes of ion-molecule reactions. The study of such reactions yields information about the relative proton affinities of molecules, where the proton affinity of a species, M, is defined as the negative of the enthalpy change of the reaction



It has been shown that simple gas phase ion-molecule reactions such as proton transfer proceed without activation energy.¹ If such a reaction occurs, then, it will be exothermic, while if it is endothermic it will not occur. Thus by studying reactions of the type



one can determine the relative proton affinities of the species M_1 and M_2 by observing the direction in which proton transfer occurs.

Ion cyclotron resonance spectroscopy (ICR) is ideally suited to the study of proton transfer reactions. Reactions may be studied at essentially thermal ion energies, thus assuring that endothermic reactions will not occur due to excess energy provided to the reactant species, while ion

¹A. Cassuto in "Advances in Mass Spectrometry," Vol. 2, R.M. Elliott, Ed., The MacMillan Co., N.Y., 1963, p. 296

cyclotron double resonance techniques may be used to selectively heat the various reactant ions and thus cause such endothermic reactions to occur on a selective basis. Finally, ICR can be employed over the pressure range from 10^{-8} to 10^{-1} torr, with residence times of the order of 10^{-3} seconds, thus enabling the study of reactions over the complete range of conversion.

In this study, ICR has been employed to study the proton affinities of H_2 , N_2 , CO_2 , CH_4 , C_2H_6 , and CO . The data obtained are combined with that obtained using other techniques to result in a compilation of the proton affinities of all the major species known to occur in planetary atmospheres. Such information is valuable as thermochemical data for the study of ion-molecule reactions and in the understanding of radiation chemistry, and may also be of great importance in the detailed studies of planetary atmospheres which will be undertaken within the next few years.

B. Experimental

The apparatus used in this study was the standard Varian cyclotron resonance apparatus, which has been described elsewhere.² Pressure measurements in the range from 10^{-5} to 10^{-1} torr were made using an MKS Baratron capacitance manometer, which without special calibration³ may be assumed to be accurate to $\pm 20\%$, which is sufficient for this study.

Most gases used were Matheson C.P. grade, which were often further purified using freeze-pump-thaw cycles. CD_4 and C_2D_6 were obtained from Merck, Sharp, and Dohme, and were 99 mole % isotopically pure, as was $^{15}\text{N}_2$ obtained from Bio-Rad Laboratories.

The general procedure for these experiments was as follows: A mixture of two or more gases, including a potential source of protons, was prepared to $\pm 20\%$ of a desired composition. The ionic composition in the mixture was studied as a function of pressure, first at an electron energy of 70 eV and then at a low electron energy (10 - 20 eV), the latter to minimize the possibility of vibrational excitation in the reactant ions.

The deduction of proton affinities from such studies is generally unambiguous, for at high pressures the predominant ionic species present will be M_1H^+ , where M_1 is the neutral

²See, for example, J.D. Baldeschwieler, Science, 159, 263 (1968).

³D.P. Ridge and J.L. Beauchamp, submitted to J. Chem. Phys.

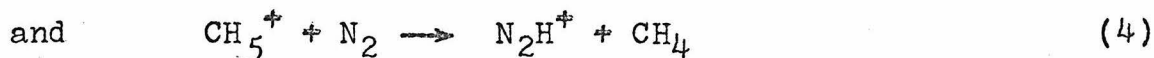
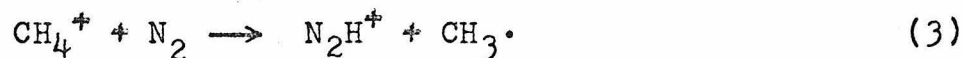
species with the highest proton affinity of those present.

Double resonance experiments were employed whenever possible to confirm suspected reactions.

C. Results of ICR Studies

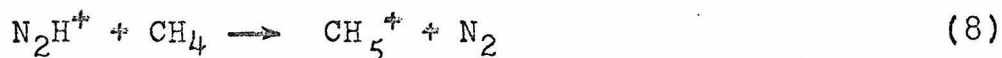
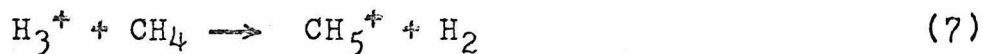
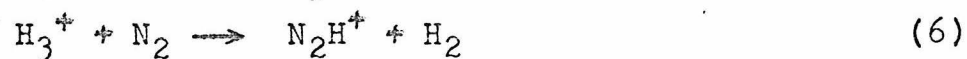


CD_4^+ is the only primary ion in a mixture of $^{15}\text{N}_2$ and CD_4 (1.5:1) studied at 15.0 eV. Under these conditions, no N_2D^+ was found despite a search up to 5×10^{-3} torr. The implication of this result is that the reactions



are both endothermic.

In order to study this system in more detail, a mixture of H_2 , $^{15}\text{N}_2$, and CH_4 (55:2.5:1) was examined at 70.0 eV. The important reactions occurring in such a mixture are



H_2^+ , CH_4^+ , and N_2^+ are, of course, also sources of CH_5^+ and N_2H^+ . This scheme is consistent with the observed ionic intensities seen in Figure I-1, from which it is clear that CH_4 has the highest proton affinity of the three species. Reactions (5) through (8) were verified as exothermic using double resonance techniques, while reaction (4) was seen to be endothermic, providing a check on reaction (8). We conclude from these studies that $\text{PA}(\text{H}_2) \leq \text{PA}(\text{N}_2) \leq \text{PA}(\text{CH}_4)$.

These results are well corroborated with those obtained by other methods. Schiff⁴ has reported reactions (5) through

⁴H.I. Schiff et al., to be published.

Figure I-1:

Mass corrected ion intensities vs. pressure in a 55:1.5:1 mixture of H_2 , $^{15}N_2$, and CH_4 examined at 70.0 V electron energy.

(Mass corrected is here defined as the normalized ratio of observed intensity to mass, that is, $(I_i/m_i)/(\sum I_i/m_i)$.)

MODEL

DATE

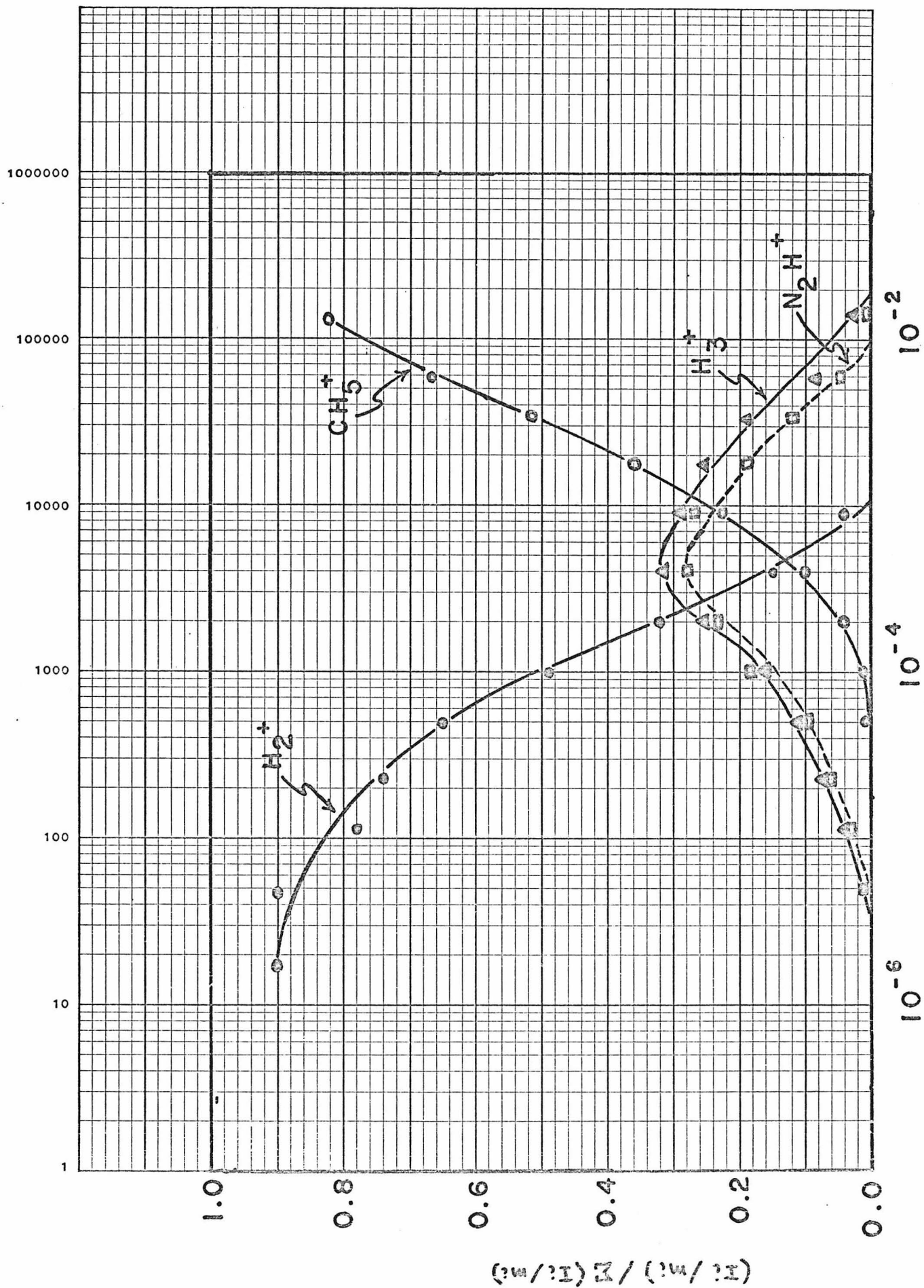
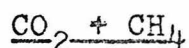
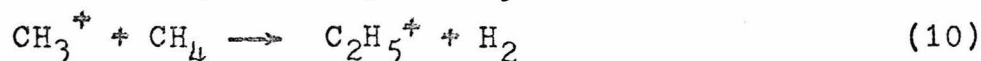
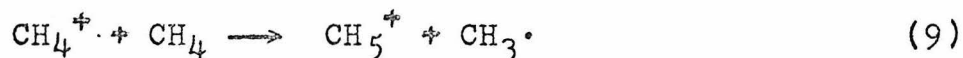


Figure I-1: Ionic Composition vs. Pressure (Torr) for H₂ + N₂ + CH₄ at 70 eV

(8) in flowing afterglow studies. Aquilanti and Volpi^{5,6} have reported reactions (5) through (7) in their high-pressure mass spectrometry work. Shannon and Harrison,⁷ also using mass spectrometric techniques, reported the occurrence of reaction (3), but this result, based on rather tenuous grounds to begin with, could certainly be explained by noting that the average primary ion energy at the exit slit in their experiments was 3.7 eV, far in excess of the amount needed to overcome the endothermicity of (3).



Mixtures of CO₂ and both CH₄ and CD₄ were studied at 70.0 eV. In both, important reactions include the standard methane reactions



as well as the mixed reactions

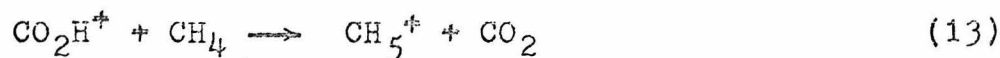
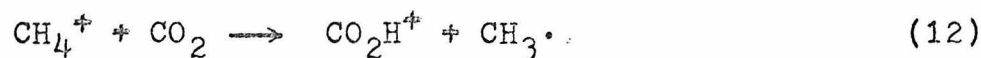
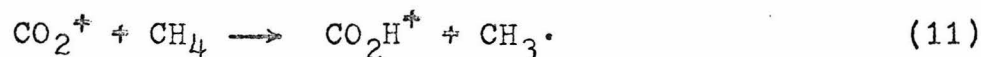


Figure I-2 is a plot of the ionic composition of a mixture of CH₄ and CO₂ vs. pressure. The disappearance of CO₂H⁺ at high pressures and the dominance of CH₅⁺ are clear evidence for (13). All of the above reactions were verified by double resonance, as was the endothermicity of proton transfer from CH₅⁺ to CO₂.

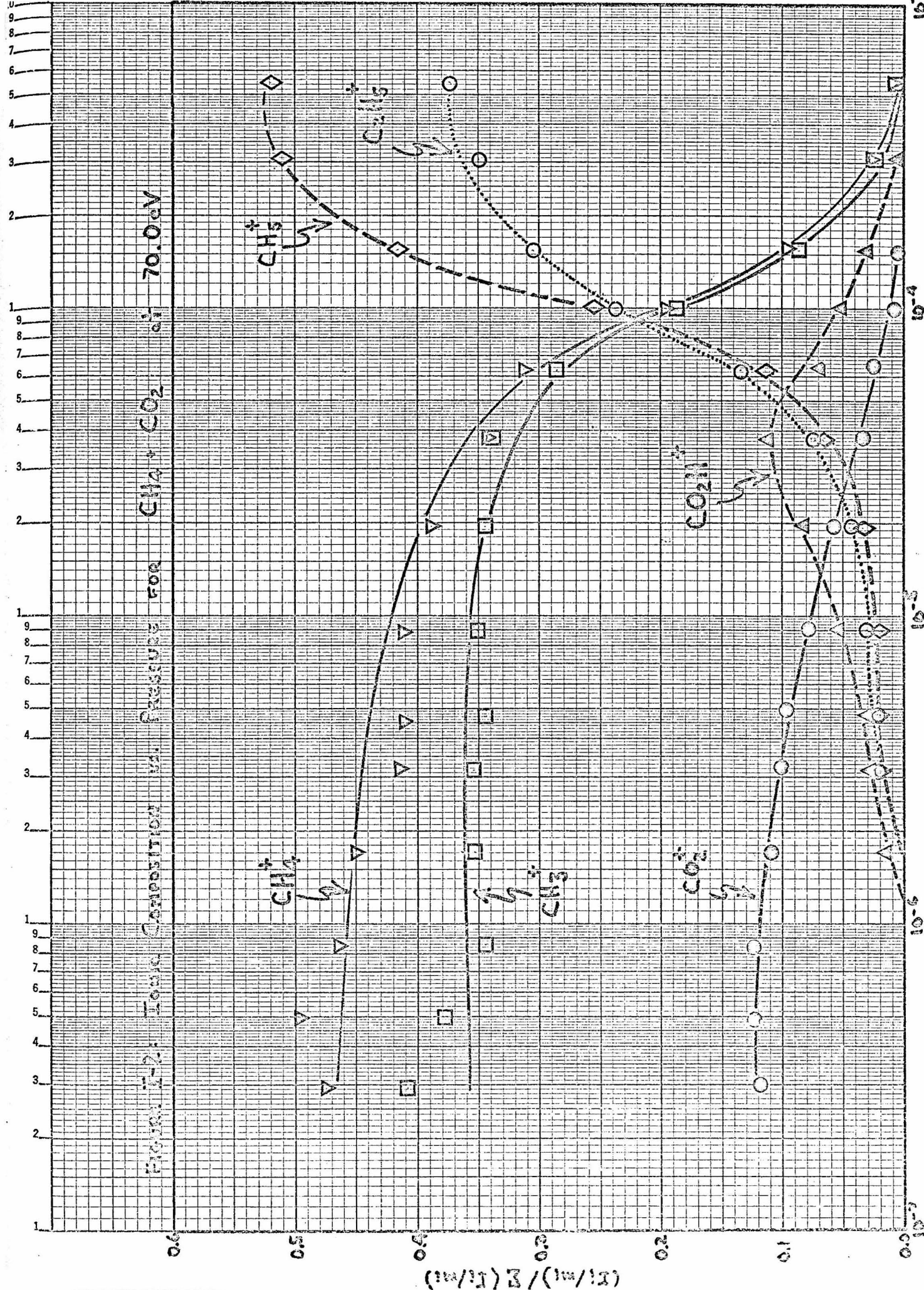
⁵V. Aquilanti and G.G. Volpi, J. Chem. Phys. 44, 2307 (1966)

⁶V. Aquilanti, A. Galli, A. Giardini-Guidoni, and G.G. Volpi, J. Chem. Phys. 43, 1969 (1965).

⁷T.W. Shannon and A.G. Harrison, J. Chem. Phys. 43, 4201 (1965).

Figure I-2:

Mass corrected ion intensities vs. pressure in a 4:1 mixture of CH_4 and CO_2 examined at 70.0 V electron energy.

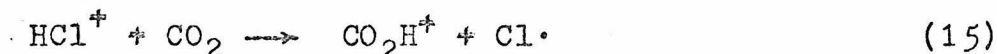
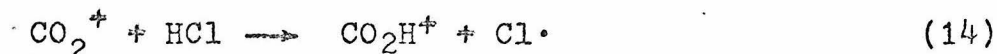


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Again, these results are supported by other techniques. Reactions (9) and (10) are well-known. Shannon and Harrison⁷ reported both (11) and (12), although as in their studies of N₂ and CH₄ they did not attain high enough pressures to observe proton transfer to CH₄ (Reactions (8) and (13)).

CO₂ + HCl

A mixture (1:1) of these two gases was examined at both 70.0 and 20.0 eV. A plot of the former study is seen in Figure I-3, from which it is evident that HCl has the higher proton affinity. Of more importance in the determination of $\Delta H_f^0(\text{CO}_2\text{H}^+)$ is the identification of the source of that species. Two reactions are possible:



Reaction (15) was verified as exothermic with double resonance (Figure I-4), suggesting⁸ that $\text{PA}(\text{CO}_2) \gg 123$ kcal/mole.

Reaction (14) could not be so verified due to the proximity of the masses of reactant and product, but may be inferred from the disappearance of CO₂⁺, which occurs far too rapidly to be the result of non-resonant charge transfer, a process known to occur with an extremely small cross-section.

N₂ + HCl

A mixture of N₂ and HCl (2:1) was examined at both 70.0 and 20.0 eV. At the lower electron energy, although

⁸Table I-2 provides a listing of the standard heats of formation used throughout this study.

Figure I-3:

Mass corrected ion intensities vs. pressure in a 1:1
mixture of HCl and CO₂ examined at 70.0 V electron energy.

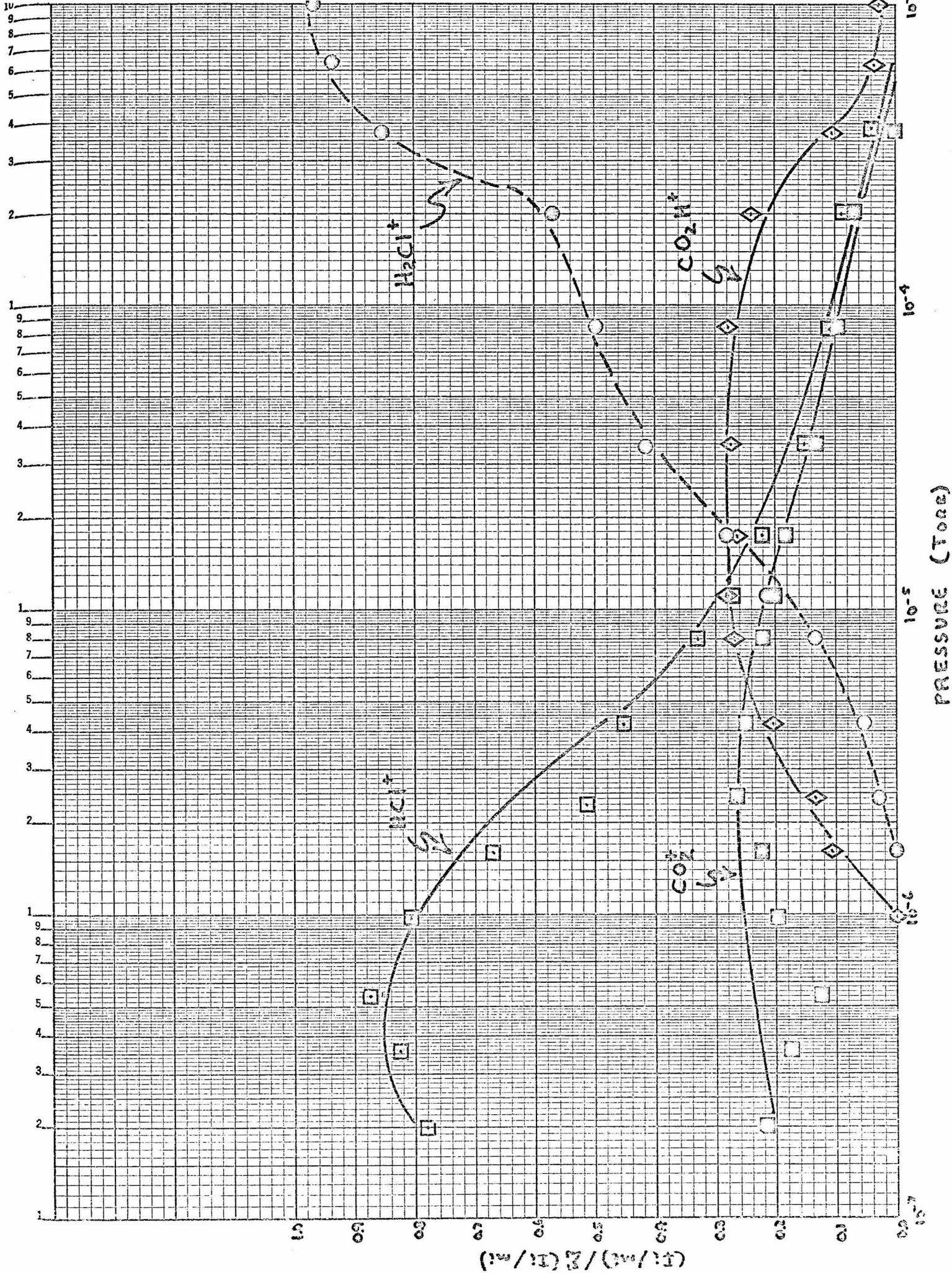


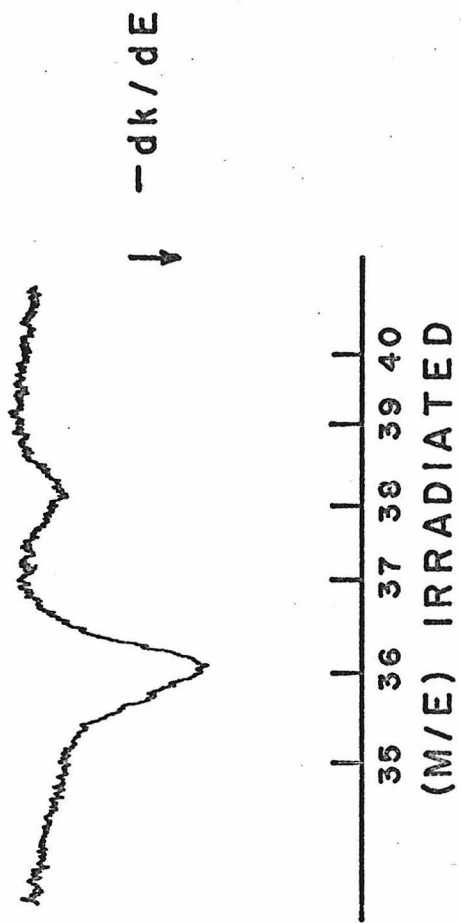
Figure I-4:

Ion cyclotron double resonance studies confirming the reaction

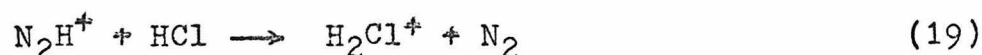
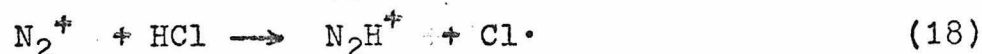
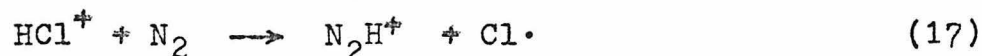
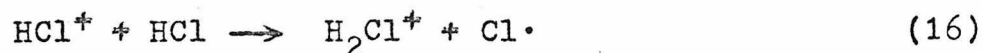


Observed at 70 V electron energy, 4×10^{-5} torr total pressure, and 10 mV irradiating power.

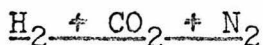
OBSERVE CO_2H^+



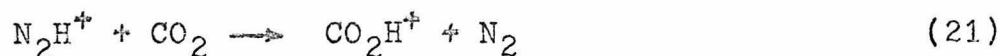
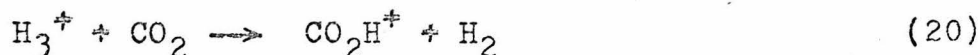
nominally above the ionization potential of N_2 , no N_2^+ was detected, and the formation of N_2H^+ was not observed. N_2H^+ is formed at 70.0 eV, but disappears at higher pressures as H_2Cl^+ becomes the dominant ion. Pertinent reactions are:



The studies at low electron energy are proof that (17) does not occur and that (16) is a major reaction. At 70.0 eV, the appearance of significant amounts of N_2H^+ must be the result of (18), while the subsequent disappearance of that ion clearly indicates the exothermicity of (19). We conclude that $PA(N_2) \leq 123$ kcal/mole.



A mixture of H_2 , N_2 , and CO_2 (98:1.5:0.5) was studied at 19.0 eV. The important reactions in this system are (5), (6), and



A plot of the ionic composition of this mixture vs. pressure (Figure I-5) indicates that all of these reactions are exothermic, a conclusion that is verified with double resonance experiments. Reaction (21) could be seen proceeding in the reverse direction only upon translational excitation of the CO_2H^+ with double resonance (Figure I-6), confirming the endothermicity of this process for unexcited CO_2H^+ .

Figure I-5:

Mass corrected ion intensities vs. pressure in a 98:1.5:0.5 mixture of H_2 , N_2 , and CO_2 examined at 19.0 V electron energy.

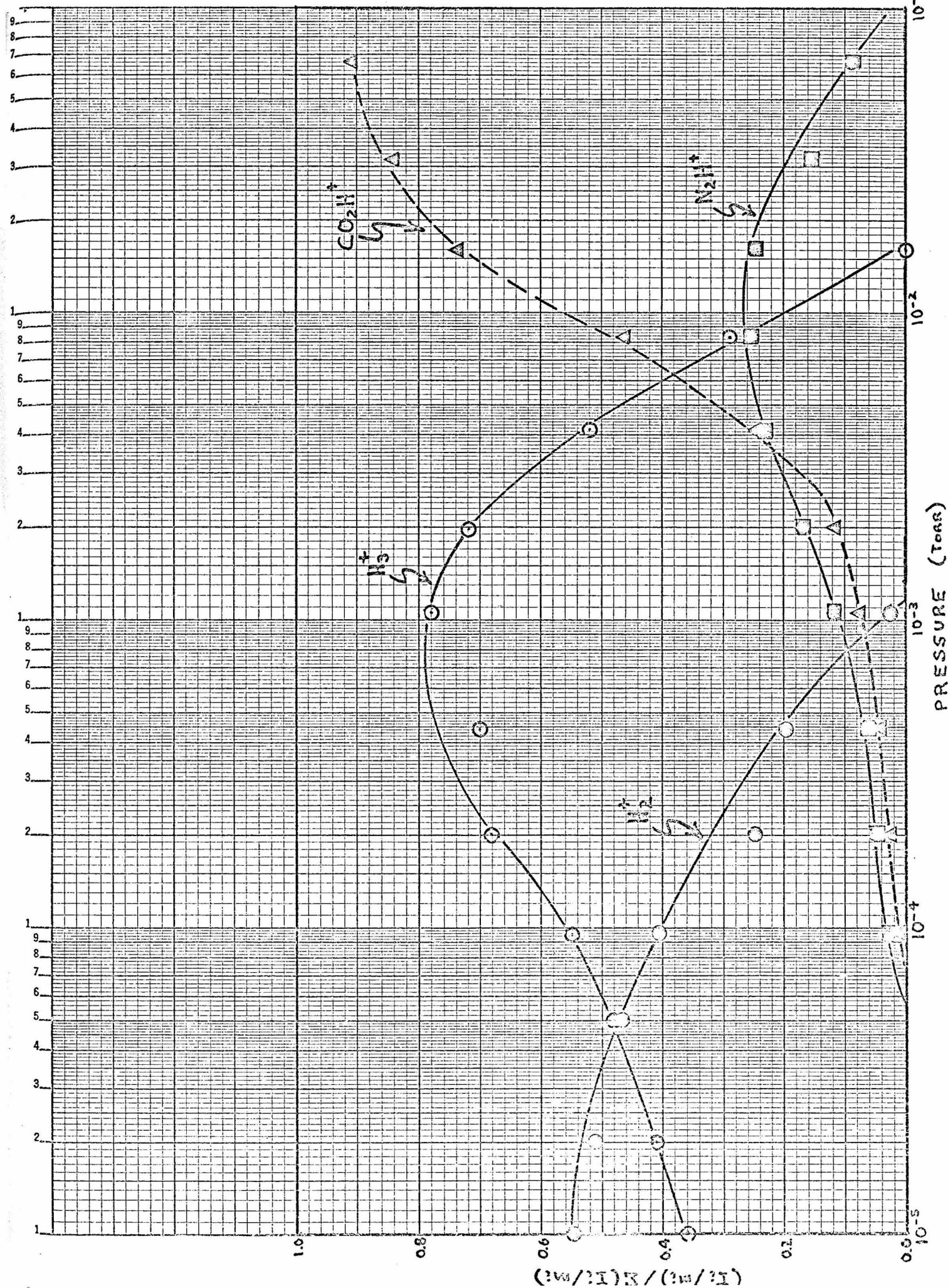


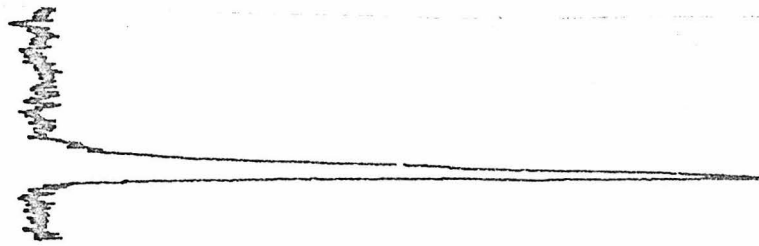
Figure I-6:

Ion cyclotron pulsed double resonance studies examining the reaction



Observed at 19 V electron energy, 4.5×10^{-4} torr total pressure in a 98:1.5:0.5 mixture of H_2 , N_2 , and CO_2 , and 25 mV irradiating power.

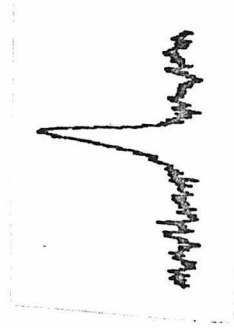
OBSERVE
 CO_2H^+



IRRADIATE
 N_2H^+

$\uparrow +$
 dk/dE
 $\downarrow -$

OBSERVE
 N_2H^+

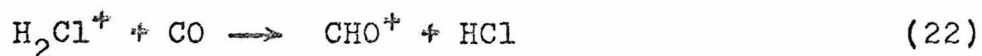


IRRADIATE
 CO_2H^+

Reactions (20) and (21) have both been reported by Schiff.⁴

CO + HCl

Recent experiments⁹ have used CHO^+ generated by electron impact on acetaldehyde to study proton transfer reactions in the alkanes. Futrell's assertion that CO has a lower proton affinity than methane and his observation of proton transfer from CHO^+ to CH_4 prompted a re-examination of the species CHO^+ . In these studies, a mixture of HCl and CO (1:1) was examined at both 70.0 and 13.0 eV. The results of the former are shown in Figure I-7, and quite clearly reveal that $\text{PA}(\text{CO}) \gg \text{PA}(\text{HCl})$, a fact which was confirmed by observance of a negative dk/dE for the reaction



$\text{PA}(\text{HCl})$ has been well established¹⁰ as 141 ± 3 kcal/mole by Haney and Franklin, who also¹¹ set $\text{PA}(\text{CO}) = 142 \pm 3$ kcal/mole.

There has been considerable discussion in the literature¹²⁻¹⁵ with regard to the reactions and heat of formation of CHO^+ . The presence of vibrational excitation in this species is a conclusion offered elsewhere by Futrell himself,¹² and coupled with the nominal 0-0.3 eV translation energy also present must

⁹J.H. Futrell et al., J. Chem. Phys. 52, 3655 (1970).

¹⁰M.A. Haney and J.L. Franklin, J. Phys. Chem. 73, 4328 (1969).

¹¹M.A. Haney and J.L. Franklin, Trans. Far. Soc. 65
1794 (1969)

¹²J.H. Futrell and T.O. Tiernan, J. Chem. Phys. 51, 5183 (1969).

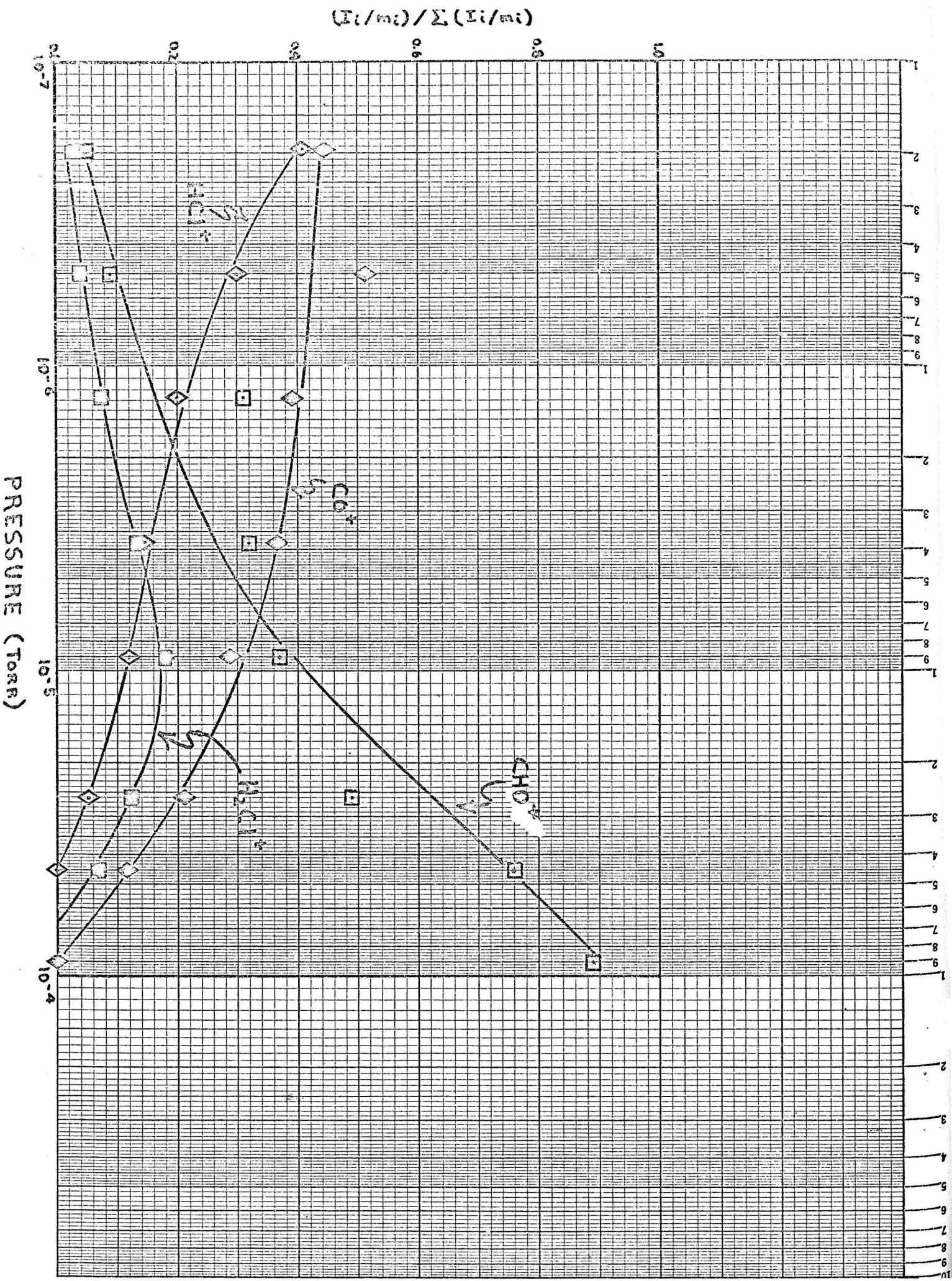
¹³H. Pritchard and A.G. Harrison, J. Chem. Phys. 48, 2827 (1968).

¹⁴H. Pritchard and A.G. Harrison, J. Chem. Phys. 48, 5623 (1968).

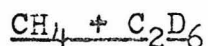
¹⁵F.H. Dorman, J. Chem. Phys. 50, 1042 (1969).

Figure I-7:

Mass corrected ion intensities vs. pressure in 1:1 mixture of CO and HCl examined at 70.0 V electron energy.

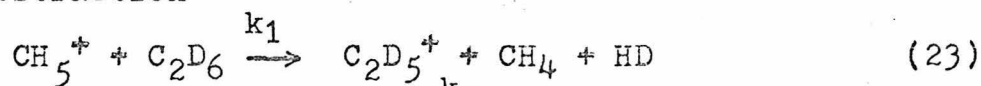


account for the reactions reported by Futrell.⁹

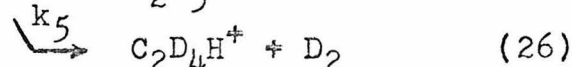
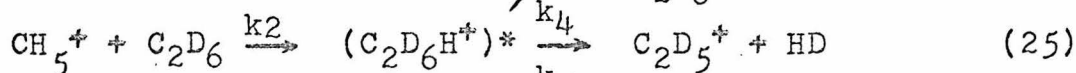
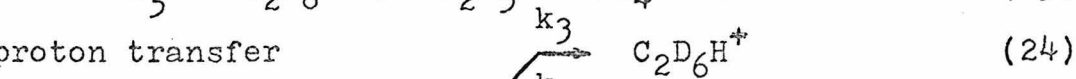


Because the CHO^+ used in the studies of Futrell seems to have contained excess energy, a re-examination of the reactions of ethane was also undertaken. Significant amounts of protonated ethane have been reported at least three times: by Futrell,⁹ who found a maximum of 42% of this ion as opposed to 58% of the dissociated products; by Munson and Field,¹⁶ who report roughly 2:1 C_2H_5^+ to C_2H_7^+ as a result of proton transfer from CH_5^+ ; and by Aquilanti and Volpi,⁵ who find about 3:1 for the same ratio using proton transfer from H_3^+ .

The results of our studies are seen in Figure I-8. The reactions we need to concern ourselves with are dissociative hydride abstraction



and proton transfer



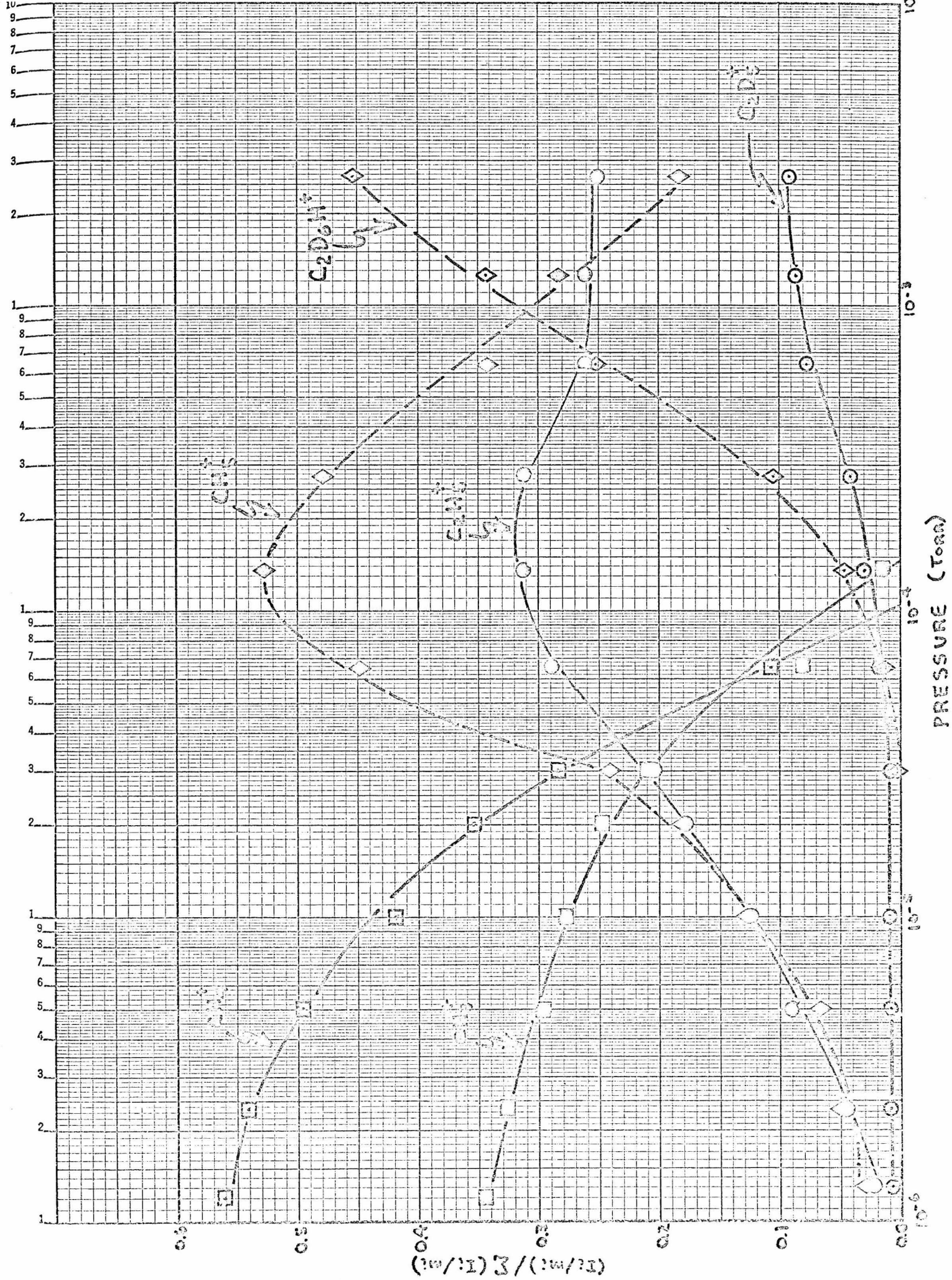
The first thing that is apparent from Figure I-8 is that the amount of protonated ethane in this study is far in excess of that obtained previously. In order to understand the significance of this observation it is first necessary to evaluate the relative importance of (23) vs. (25)

Although the amount of $\text{C}_2\text{D}_4\text{H}^+$ is not seen in Figure I-8, the observed ratio $\text{C}_2\text{D}_5^+/\text{C}_2\text{D}_4\text{H}^+$ is approximately 3.3:1.

¹⁶M.S.B. Munson and F.H. Field, J. Am. Chem. Soc. 87, 3294 (1965).

Figure I-8:

Mass corrected ion intensities vs. pressure in a 49:1 mixture of CH_4 and C_2D_6 examined at 20.0 V electron energy.



A certain amount of this $C_2D_5^+$ results from the primary ionization of C_2D_6 at 20.0 eV, which can be estimated by noting that in pure C_2H_6 at 20.0 eV, $[C_2H_5^+] \approx [C_2H_6^+]$ over the range of pressures from 10^{-6} to 10^{-3} torr.¹⁷ After correcting for this, $(k_1 + k_4)/k_5$ is estimated to be 1.9.

If one considers the decomposition of $(C_2D_6H^+)^*$, there are 15 ways to lose D_2 and only 6 ways to lose HD, thus predicting $k_4/k_5 = 0.4$. If both atoms are lost from the same carbon atom and no scrambling occurs, $k_4/k_5 = 1.0$. Even allowing for an isotope effect, it seems clear that $k_4/k_5 < (k_1 + k_4)/k_5$, and hence k_1 is non-zero, that is, dissociative hydride abstraction does in fact occur.

Ions in ICR experiments are nominally at thermal energies, and under such conditions it is clear that $C_2D_6H^+$ is stable with respect to decomposition. When H_3^+ is used as the protonating agent as in the experiments of Aquilanti and Volpi,⁵ the extra exothermicity supplied by the difference in the proton affinities of H_2 and CH_4 is undoubtedly deposited to a great extent in the $C_2D_6H^+$, lessening the probability of collisional stabilization (24). We have already observed that the CHO^+ ions in Futrell's experiments were energetic enough to transfer a proton to CH_4 , which would explain the predominance of dissociative products observed in those studies. Munson and Field¹⁶ used CH_5^+ as a protonating agent as was the case in this work, but their studies were done at an electron energy of 150 eV, a repeller field strength of 6.25 V/cm., and an ion path length of 2.0 mm. A maximum ion energy of 1.25 eV

¹⁷S.L. Patt, unpublished results.

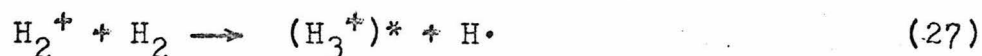
was therefore attainable, easily enough to bring about the decomposition of $C_2D_6H^+$.

Double resonance studies are likely to be important in this regard, because of the selective excitation that they allow. Double resonance spectra of $C_2D_4H^+$ and $C_2D_5^+$ indicate that both of these ions are formed in increasing numbers upon translational excitation of $C_2D_6H^+$. The formation of $C_2D_6H^+$ is seen to be exclusively from CH_5^+ . In addition, both $C_2D_4H^+$ and $C_2D_5^+$ show a positive dk/dE from CH_5^+ . It is not immediately clear whether this represents only an increasing tendency of $C_2D_6H^+$ to fall apart as a result of the increased energy supplied to it by the excited CH_5^+ , or whether in addition dissociative hydride abstraction (23) is becoming more important at higher ion energies. Double resonance results quantitative enough to clarify this point could not be obtained.

D. Discussion

H₂

Ion-molecule reactions of hydrogen, particularly those of the H₃⁺ ion, have been well studied.^{4-6,18-21} A list of the reported reactions, along with the thermochemical inferences that can be drawn from them, is provided in Table I-1. In interpreting these results, it is important to bear in mind the recent findings of Elleman²¹ regarding the nature of H₃⁺ in these reactions; he finds that an accurate representation of the situation is



At low pressures, then, one is liable to find a completely different reactivity for the H₃⁺ ion than at high pressures when collisional de-activation can occur. An alternative explanation for the same phenomena is that the transfer of a proton from H₃⁺ can result in both v=0 and v=1 H₂ being produced.

A good example of this phenomenon is found in the work of Aquilanti and Volpi.⁵ In studies of the reactions of H₃⁺ with CH₄ and C₂H₆, they found that as the pressure of H₂ was reduced, the yield of protonated alkane vs. the dissociation product (CH₃⁺ and C₂H₅⁺, respectively) approached zero, that

¹⁸J.T. Armstrong, undergraduate research thesis at the California Institute of Technology, unpublished (1969).

¹⁹V. Aquilanti, A. Galli, and G.G. Volpi, J. Chem. Phys. 47, 831 (1967).

²⁰F.C. Fehsenfeld, A.L. Schmeltekopf, and E.E. Ferguson, J. Chem. Phys. 46, 2802 (1967).

²¹D.D. Elleman and M.T. Bowers, J. Am. Chem. Soc. 92, 1847 (1970)

Table I-1. Reactions of the H_3^+ Ion

Neutral Reactant	Products	Reference	Inference
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_4 \end{array}$	$\text{CH}_5^+ + \text{H}_2$	18,5	$\text{PA}(\text{H}_2) \leq 126$
	$\text{CH}_3^+ + 2\text{H}_2$	5	Reactant must be $(\text{H}_3^+)^*$
C_2H_4	$\text{C}_2\text{H}_5^+ + \text{H}_2$	18,4,19	$\text{PA}(\text{H}_2) \leq 159$
	$\text{C}_2\text{H}_3^+ + 2\text{H}_2$	18,4,19	$\text{PA}(\text{H}_2) \leq 111$
C_2H_6	$\text{C}_2\text{H}_7^+ + \text{H}_2$	19,5,4	$\text{PA}(\text{H}_2) \leq 130$
	$\text{C}_2\text{H}_5^+ + 2\text{H}_2$	19,5,4	$\text{PA}(\text{H}_2) \leq 127$
$\begin{array}{c} \text{CH} \\ // \quad \backslash \\ \text{CH}_2 \quad \text{CH}_3 \end{array}$	$\text{C}_3\text{H}_7^+ + \text{H}_2$	19	$\text{PA}(\text{H}_2) \leq 162$
	$\text{C}_3\text{H}_5^+ + 2\text{H}_2$	18,19	$\text{PA}(\text{H}_2) \leq 155$
	$\text{C}_2\text{H}_3^+ + \text{CH}_4 + \text{H}_2$	18,19	$\text{PA}(\text{H}_2) \leq 121$
$\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \backslash \quad / \\ \text{CH}_2 \end{array}$	$\text{C}_3\text{H}_5^+ + 2\text{H}_2$	18	$\text{PA}(\text{H}_2) \leq 163$
	$\text{C}_2\text{H}_3^+ + \text{CH}_4 + \text{H}_2$	18	$\text{PA}(\text{H}_2) \leq 129$
C_3H_8	$\text{C}_3\text{H}_7^+ + \text{H}_2$	5	$\text{PA}(\text{H}_2) \leq 132$
	$\text{C}_2\text{H}_5^+ + \text{CH}_4 + \text{H}_2$	5	$\text{PA}(\text{H}_2) \leq 122$
C_2H_2	$\text{C}_2\text{H}_3^+ + \text{H}_2$	4	$\text{PA}(\text{H}_2) \leq 152$

References for heats of formation used in this table are listed in Table I-2.

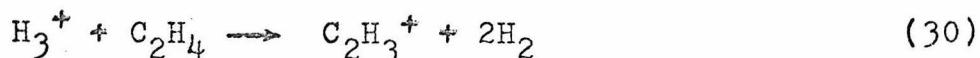
is, when $(H_3^+)^*$ reacted with methane and ethane, the protonated alkane received too much internal energy and fell apart.

The proton affinity of H_2 is established by two reactions. A lower limit on $PA(H_2)$ is set by the reaction



Schiff⁴ finds that this reaction proceeds in the reverse direction and does not proceed in the forward direction, thus, $PA(H_2) \geq PA(O_2)$. Foner and Hudson have studied the appearance potential of O_2H^+ from hydrogen peroxide^{22a,b} and from HO_2 free radical^{22c}, and obtained a consistent value of 271 ± 1 kcal/mole for $\Delta H_f^0(O_2H^+)$, or $PA(O_2) = 95 \pm 1$ kcal/mole.

An upper limit on $PA(H_2)$ is established by the reaction



This reaction, observed by both Armstrong and Aquilanti, Galli, and Volpi, would mean $PA(H_2) \leq 111 \pm 1$ kcal/mole. Studies of the relative amounts of $C_2H_4^+$ vs. $C_2H_5^+$ produced by simple proton transfer as a function of H_2 pressure¹⁹ show that $C_2H_3^+$ decreases substantially with pressure, indicating that much of it may be coming from $(H_3^+)^*$. However some $C_2H_3^+$ persists and one must conclude that (30) does in fact occur for ground state H_3^+ . We thus have $95 \text{ kcal/mole} \leq PA(H_2) \leq 111 \text{ kcal/mole}$, with a suggested value of $PA(H_2) = 103 \text{ kcal/mole}$, in substantial agreement with Schiff.⁴

²²S.N. Foner and R.L. Hudson, J. Chem. Phys.; (a) 23, 1364 (1955); (b) 36, 2676 (1962); (c) 36, 2681 (1962).

He, Ne

In order to establish the proton affinities of the rare gases, much work has been done using mixtures of these gases with hydrogen.^{6,23,24} Chupka and Russell used photoionization mass spectrometry to study the reactions



Both of these reactions are endothermic with ground-state H_2^+ , but by using photons with a resolution of ~ 0.008 eV, Chupka and Russell were able to show the onset of these reactions occurred for the $v=3$ and $v=2$ vibrational levels of H_2^+ , respectively. By making use of extremely accurate quantum mechanical calculations²⁵ to provide $\Delta H_f^\circ(\text{HeH}^+)$, they were then able to quantify the translational energy contribution to these reactions and to thus arrive at a value for $\Delta H_f^\circ(\text{NeH}^+)$ as well. The values established in this manner are $\text{PA}(\text{He}) = 42.5 \pm 1$ kcal/mole and $\text{PA}(\text{Ne}) = 48 \pm 1$ kcal/mole.

These values are consistent with the failure of He and Ne to affect the radiation-induced H-D exchange in mixture of H_2 and D_2 , a process which proceeds through ionic mechanisms.²³ Identically, they are consistent with the constant H_3^+ intensity observed in mass spectrometric studies when He or Ne are added to H_2 .⁶

²³S.O. Thompson and O.A. Schaeffer, J. Am. Chem. Soc. 80, 553 (1958).

²⁴W.A. Chupka and M.E. Russell, J. Chem. Phys. 49, 5426 (1968).

²⁵L. Wolniewicz, J. Chem. Phys. 38, 1651 (1963).

Ar

When Ar is added to H_2 in a mass spectrometer, the observed concentration of H_3^+ increases.⁶ As H_2 is added to Ar, Ar^+ decreases rapidly, ArH^+ builds up and then decreases, and H_3^+ builds up to a maximum. These observations are consistent with the reactions



There has been some question in the past²⁶ about the occurrence of



In their recent studies, Chupka and Russell²⁴ seem to have provided a definitive answer — reaction (35) does occur, and it does so with ground state H_2^+ . This reaction, then, sets $PA(Ar) \geq 62$ kcal/mole, while (34) means that $PA(Ar) \leq 103$ kcal/mole. One might suggest, then, that $PA(Ar) = 82 \pm 20$ kcal/mole. The value of 70 kcal/mole provided by the calculations of Moran and Friedman²⁷ is seen to be within those limits.

Kr

The reactions of Kr have been considered by several authors.^{6,28,29} The production of KrH^+ in mixtures of H_2 and Kr was observed by all of them, and in each case attributed to the reaction

²⁶See, for example, T.W. Shannon and A.G. Harrison, J. Chem. Phys. 43, 4206 (1965).

²⁷T.F. Moran and L. Friedman, J. Chem. Phys. 40, 860 (1964).

²⁸D.P. Stevenson and D.O. Schissler, J. Chem. Phys. 29, 282 (1958)

²⁹M.S.B. Munson and F.H. Field, J. Am. Chem. Soc. 87, 4242 (1965)



despite the fact that



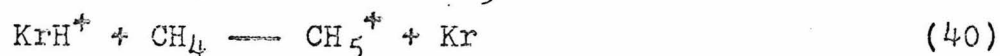
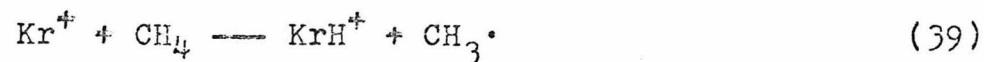
is more exothermic by 33 kcal/mole.

Aquilanti et al.⁶ found that when Kr was added to H_2 , no change was observed in the H_3^+ intensity. As H_2 was added to Kr, Kr^+ rapidly decreased to be replaced by KrH^+ . They interpreted this as evidence for (36), and decided that



must be extremely slow, if it occurs at all in either direction. Stevenson and Schissler²⁸ showed that by decreasing the electron energy below the ionization potential of H_2^+ they could confirm (36), although their data does not seem to rule out the occurrence of (37) at higher electron energies. Munson and Field²⁹ also found KrH^+ in such a mixture, although their experiments did not provide any information as to the source of that species.

Munson and Field also studied the reactions of Kr with CH_4 . The results they obtained showing a buildup and then a decrease of KrH^+ suggest the following sequence:



Both reactions (36) and (39) suggest that $\text{PA}(\text{Kr}) \gg 94$ kcal/mole, while (40) gives the unambiguous result that $\text{PA}(\text{Kr}) < \text{PA}(\text{CH}_4)$. The evidence of Aquilanti et al. seems to require both that reaction (37) not occur to any great extent, and that $\text{PA}(\text{Kr}) \approx \text{PA}(\text{H}_2) = 103$ kcal/mole. It is still not at all clear why (37) is not seen. Using the charge-

induced dipole interaction model of Gioumousis and Stevenson,³⁰ one can calculate that H_2^+ should react with Kr 1.23 times faster than it does with Ar. One can speculate only that charge exchange, which is exothermic for (41) while being



endothermic for the corresponding reaction with Ar, must play a role in this observation.

Xe.

Xe causes a sharp decrease⁶ in H_3^+ intensity when added to H_2 , and a corresponding increase in XeH^+ , so that $\text{PA}(\text{Xe}) \geq \text{PA}(\text{H}_2)$. Munson and Field²⁹ studied Xe in CH_4 and found that CH_5^+ did not decrease after reaching its maximum intensity, thus, $\text{PA}(\text{Xe}) \leq \text{PA}(\text{CH}_4)$. Tiernan and Gill³¹, using a tandem mass spectrometer, found that the predominant (> 90%) reaction of Xe^+ with CH_4 was charge transfer, while the reaction of CH_4^+ with Xe to yield XeH^+ constituted ~ 33% of the reactions of CH_4^+ with Xe. As a result, one may say that $123 \text{ kcal/mole} \leq \text{PA}(\text{Xe}) \leq \text{PA}(\text{CH}_4)$.

NO, NO₂, and N₂O

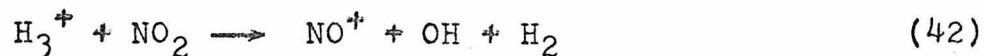
The various oxides of nitrogen have all received at least some study.^{4,29} Munson and Field observed no HNO^+ in a mixture of CH_4 and 1% NO, and concluded that proton transfer from CH_5^+ to NO does not occur. Schiff, using

³⁰G. Gioumousis and D.P. Stevenson, J. Chem. Phys. 29, 294 (1958). See part II of this thesis for further detail. All polarizabilities taken from E.W. Rothe and R.B. Bernstein, J. Chem. Phys. 31, 1619 (1959)

³¹T.O. Tiernan and P.S. Gill, J. Chem. Phys. 50, 5042 (1969).

flowing afterglow techniques, found HNO^+ as the major product of the reaction of H_3^+ with NO . These two observations imply that $\text{PA}(\text{H}_2) \leq \text{PA}(\text{NO}) \leq \text{PA}(\text{CH}_4)$.

Schiff also studied NO_2 , and found a major reaction to be



No HNO_2^+ was found, but HNO_2^+ is unstable with respect to decomposition to $\text{NO}^+ + \text{OH}$ unless $\text{PA}(\text{NO}_2) \geq 130$ kcal/mole. Thus no conclusion may be reached on the basis of (42).

In studies⁴ of N_2O , evidence of proton transfer to that species from both H_3^+ and N_2H^+ (arising from an N_2 impurity) was found. Thus, $\text{PA}(\text{N}_2\text{O}) \geq \text{PA}(\text{N}_2)$

N_2

The limits on the proton affinity of N_2 are not as well defined as they might be. Observation of proton transfer from H_3^+ (6) sets the lower limit, while the failure to observe reactions (3) and (17) sets an upper limit:

$\text{PA}(\text{H}_2) \leq \text{PA}(\text{N}_2) \leq 123$ kcal/mole. The fact that CO_2H^+ will transfer a proton to N_2 upon mild translational excitation with double resonance indicates that $\text{PA}(\text{N}_2)$ is probably somewhat closer to the upper limit: $\text{PA}(\text{N}_2) = 118 \pm 5$ kcal/mole. The reaction of N_2H^+ with C_2H_4 in analogy with (30) would shed further light on this question.

CO_2

Reactions (12) and (15) both suggest a lower limit on the proton affinity of CO_2 of 123 kcal/mole, while proton transfer to CH_4 implies $\text{PA}(\text{CO}_2) \leq \text{PA}(\text{CH}_4)$. We suggest a value of 125 kcal/mole for $\text{PA}(\text{CO}_2)$ in substantial agreement

with appearance potential measurements¹¹ of CO_2H^+ from formic and acetic acids.

CH_4

Reaction (9) requires that the proton affinity of CH_4 be greater than 123 kcal/mole. An upper limit on $\text{PA}(\text{CH}_4)$ is provided by the studies with ethane, where the occurrence of at least some dissociative hydride abstraction (23) means that $\text{PA}(\text{CH}_4) \leq 127$ kcal/mole. Since $\text{PA}(\text{CH}_4) > \text{PA}(\text{CO}_2)$, 126 kcal/mole for the former and 125 kcal/mole for the latter seem to be a reasonable choice.

$\text{C}_2\text{H}_2, \text{C}_2\text{H}_4$

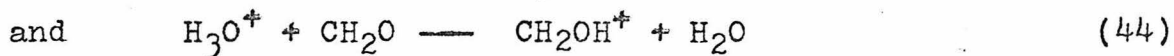
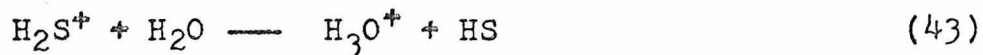
The proton affinities of these species are accurately established from appearance potentials from more saturated hydrocarbons, and the values seen in Table I-2 imply that $\text{PA}(\text{C}_2\text{H}_2) = 152 \pm 1$ kcal/mole, while $\text{PA}(\text{C}_2\text{H}_4) = 159 \pm 3$ kcal/mole.

C_2H_6

It was concluded above that the decomposition of C_2H_7^+ to C_2H_5^+ must be endothermic, and thus $\text{PA}(\text{C}_2\text{H}_6) > 127$ kcal/mole. Since this decomposition occurs readily, both with double resonance in this work and excess ion energy in other studies, we suggest with Futrell⁹ that the endothermicity is perhaps 3 kcal/mole, or $\text{PA}(\text{C}_2\text{H}_6) = 130 \pm 3$ kcal/mole.

H₂O, NH₃, HCN

The many ion-molecule reactions involving H₃O⁺ have been extensively discussed by Beauchamp and Buttrill.³² The limiting reactions found were



These reactions set PA(H₂O) = 165 ± 4 kcal/mole. More recent studies by Haney and Franklin³³ using appearance potential studies in which excess energies of the ionic fragments were accounted for gave exactly the same result. Similar experiments^{11,33} yield PA(NH₃) = 207 ± 3 kcal/mole and PA(HCN) = 170 ± 3 kcal/mole.

³²J.L. Beauchamp and S.E. Buttrill, Jr., J. Chem. Phys. 48, 1783 (1968).

³³M.A. Haney and J.L. Franklin, J. Chem. Phys. 50, 2028 (1969).

E. Summary

In Table I-2 are summarized the data which have been assembled in this study. The proton affinity, hydrogen affinity (Defined as the negative of the enthalpy change for the reaction $M^+ + H \rightarrow MH^+$), and the ionization potential of the major species found in the planetary atmospheres of this solar system are listed.

These data have potentially important consequences in the study of planetary atmospheres. Given some source of hydrogen atoms and some ionized species, ion-molecule reactions of the type discussed in this work will occur, and the species that will be observed can be predicted on the basis of these data. For example, recent studies³⁴ have shown that the proton bound dimer of water, $(H_2O)_2H^+$ is the dominant ionic species in the D region of the ionosphere at altitudes below 80 km. Kebarle³⁵ has analyzed the sequence of reactions leading to the formation of this species, but the important thing to note from Table I-2 is that H_2O has a higher proton affinity than any other neutral species present — if it did not, one would not detect the proton bound dimer.

Proton transfer reactions are potentially an extremely sensitive mechanism for the detection of species present in small amounts. The atmosphere of Jupiter, for example,

³⁴R.S. Narcisi and A.D. Bailey, J. Geophys. Res. 70, 3787 (1965).

³⁵A. Good, D.A. Durden, and P. Kebarle, J. Chem. Phys. 52, 222 (1970).

Table I-2. Proton Affinities, Hydrogen Affinities, and Ionization Potentials of Atmospheric Gases

Species (M)	IP(M) eV	$\Delta H_f^0(M)$	$\Delta H_f^0(M^+)$	$\Delta H_f^0(MH^+)$	PA(M)	HA(M)
<u>kcal/mole</u>						
He	24.58	0	567	324	42 ± 1	295
Ne	21.56	0	497	318	48 ± 1	232
Ar	15.76	0	363	284	82 ± 20	132
Kr	14.00	0	323	263	103 ± 5	112
Xe	12.13	0	280	242	124 ± 3	90
H ₂	15.44	0	356	263	103 ± 5	145
N ₂	15.57	0	359	248	118 ± 5	163
O ₂	12.06	0	278	271	95 ± 1	59
CO	14.02	-26.4	297	197	143 ± 3	152
NO	9.25	21.6	235	273	115 ± 10	14
CO ₂	13.75	-94.1	223	147	125 ± 2	128
NO ₂	9.76	7.9	233	??	?	?
(PA < 103?)						
HCN	13.82	32.3	351	228	170 ± 5	175
H ₂ O	12.59	-57.8	233	143	165 ± 4	142
NH ₃	10.15	-11.0	223	148	207 ± 3	127
CH ₄	12.75	-17.9	276	222	126 ± 2	106
C ₂ H ₂	11.40	54.2	317	268	152 ± 1	101
C ₂ H ₄	10.43	12.5	253	219	159 ± 3	86
C ₂ H ₆	11.50	-20.2	245	216	130 ± 3	81

Table I-2 Continued. Additional Thermochemical Data

<u>Species (M)</u>	<u>$\Delta H_f^\circ(M)$</u>
	<u>kcal/mole</u>
H	52.1
CH ₃	33.2
Cl	29.1

Heats of formation of neutrals taken from:

Wagman, D.D, Evans, W.H., Parker, V.B. Halow, I., Bailey, S.M., and Schumm, R.H.,
NBS Tech. Note 270-3 (U.S. Government Printing Office, Washington, D.C., 1968).

Ionic heats of formations taken from:

Franklin, J.L., Dillard, J.G., Rosenstock, H.M., Herron, J.T., Draxl, K.,
and Field, F.H., "Ionization Potentials, Appearance Potentials and Heats of
Formation of Gaseous Positive Ions," NSRDS-NBS 26 (U.S. Government Printing
Office, Washington, D.C., 1969)

With the exception of $\Delta H_f^\circ(C_2H_3^+)$:

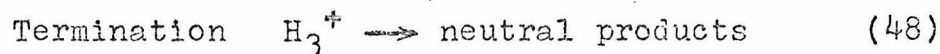
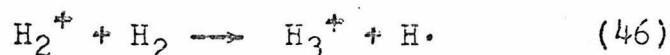
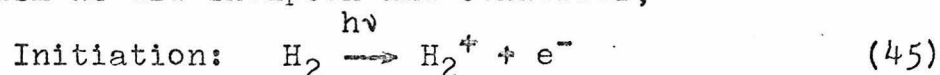
B. Brehm, Z. Naturforsch, 21a, 196 (1966); and W.A. Chupka, M.E. Russell,
and K. Refaey, J. Chem. Phys. 48, 1518 (1968)

And $\Delta H_f^\circ(C_2H_5^+)$ which comes from

W.A. Chupka and J. Berkowitz, J. Chem. Phys. 47, 2921 (1967)

is thought to consist mostly of H_2 with smaller amounts of NH_3 and CH_4 .³⁶ The predominant species in the ionosphere is expected to be NH_4^+ , a prediction which will soon be experimentally verifiable. In the same way, detection of the protonated species might offer a means of detecting small quantities of either H_2O or NH_3 on Mars.

There are other important applications of this work. For example, it was the work of Thompson and Schaeffer²³ discussed herein which led to the knowledge that the radiation induced isotopic exchange in gaseous hydrogen-deuterium mixtures proceeds almost exclusively through an ionic chain mechanism. The complete suppression of such exchange upon the addition of small amounts of Xe, and the mild suppression of the exchange with small amounts of Kr can readily be understood on the basis of the proton affinities of Xe and Kr. If we write the mechanism as did Thompson and Schaeffer,



we can see that Kr will compete with H_2 in (46), with the KrH^+ that is formed being unreactive as we saw above. Xe can interfere with both (46) and (47) to form the stable XeH^+ .

³⁶W.T. Huntress, Jr. (private communication).

The use of proton-transfer reactions for the sensitive detection of species in extra-terrestrial atmospheres was discussed above. These same principles form the basis of a new apparatus called the plasma chromatograph,³⁷ which has been used in the analysis of atmospheric impurities as low as 0.1 parts per billion. Basically, this device makes use of the fact that the proton affinities of most organic species (those studied in this work being the exception) are above that of water. $(H_2O)_n^+ H^+$ ions are generated, and the organic species are detected after proton transfer to them has occurred.

The study of proton-transfer reactions and the determination of proton affinities of molecules is, then, an extremely fruitful area.

³⁷F.W. Karasek, Research/Development 21, 34 (March, 1970)

II. REACTION RATES AND ION-MOLECULE REACTIONS OF THE ALKYL HALIDES

INTRODUCTION:

The study of reaction rates is an extremely important part of the study of ion-molecule reactions in general. The determination of relative reaction rates provides a measure of the importance of various reaction channels in a given system, and also provides a comparison of similar reactions in different systems. Absolute reaction rates may be compared with theoretical predictions, thus providing an estimate of the validity of different reaction models. In short, reaction rates are a valuable handle in the understanding of the mechanism of ion-molecule reactions.

The use of Ion Cyclotron Resonance Spectroscopy in the determination of reaction rates has been treated by several authors.¹⁻⁵ The most complete analysis of the subject is that of Comisarow⁵, whose treatment removed the former restrictions imposed by the low pressure³ and high pressure² limits. To employ this treatment, however, one must measure both peak heights and linewidths for the ions being considered. In this study the more simplified treatment of Marshall and Buttrill⁴ was used, together with the observation from

¹J.L. Beauchamp, Ph.D. Thesis, Harvard University (1967).

²M.T. Bowers, D.D. Elleman, and J.L. Beauchamp, J. Phys. Chem. 72, 3599 (1968).

³S.E. Buttrill, Jr., J. Chem. Phys. 50, 4125 (1969).

⁴A.G. Marshall and S.E. Buttrill, Jr., J. Chem. Phys. 52, 2752 (1970).

⁵M.B. Comisarow, to be published.

Comisarow⁵ that the error inherent in this approach will increase with pressure. For several extremely slow reactions, the high-pressure treatment described by Bowers, Elleman, and Beauchamp² was employed.

In a typical ICR experiment, ions are formed in the source region of the cell by electron impact. The ions are then caused to drift through the source and analyzer regions by the presence of crossed static electric and magnetic fields. The velocity of this motion can be calculated knowing the strength of the applied fields and the configuration of the cell.^{1,6}

As they drift down the cell, ions may undergo both reactive and non-reactive collisions with the neutral molecules present. Ions are detected in the analyzer region of the cell with a marginal oscillator detector. The calculation of the observed signal intensity for a given ion consists first in determining the number of those ions in a particular small region of the analyzer, next in calculating the power absorption from those ions, and finally in summing such contributions over the entire analyzer region. Rate constants, which are contained in the first of these steps, cannot be obtained explicitly as a function of the observed intensities, but by using a computer one can make use of iterative techniques to obtain agreement between observed and calculated intensities.

The full analysis outlined above is described in some detail by Marshall and Buttrill.⁴ Explicit solutions for the intensities are obtained for the case of primary, secondary,

⁶P. G. Miasek, research report, California Institute of Technology (1970).

and stable tertiary ions, in which only one neutral species is present and in which no ion is formed from more than one precursor ion. The expressions for primary, secondary, and tertiary ion signal intensities obtained in this manner are

$$I_p = (P(0)K_p/N^2I^2) (\exp(-NIt_p) - \exp(-NIt_p^i)) \quad (1)$$

$$-NI(t_p^i - t_p) \exp(-NIt_p^i) \quad (1)$$

$$I_{si} = (P(0)K_{si}k_i \exp(-NIt_{si})/N^2IJ_i^2(I-J_i)^2) \cdot \quad (2)*$$

$$(J_i^2 + IJ_i \exp(-NJ_i(t_{si}^i - t_{si})) - IJ_i - J_i^2 \exp(-NI(t_{si}^i - t_{si})) + I(I-J_i) \exp(-N(J_i-I)t_{si}) - I(I-J_i)(1 + NJ_i(t_{si}^i - t_{si})) \exp(-NJ_i t_{si}^i + NIt_{si}))$$

$$\text{and } I_{tj} = (P(0)K_{tj}k_i k_j / N^2 I^3 J_i^3 (I-J_i)) ((I^3 - \quad (3)$$

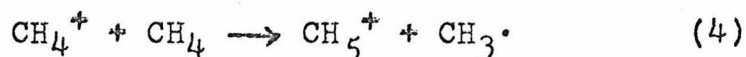
$$NI^3 J_i (t_{tj}^i - t_{tj})) \exp(-NJ_i t_{tj}) - (J_i^3 - NJ_i^3 I (t_{tj}^i - t_{tj})) \exp(-NIt_{tj}) + J_i^3 \exp(-NIt_{tj}^i) - I^3 \exp(-NJ_i t_{tj}^i) + N^2 I^2 J_i^2 (I-J_i) (t_{tj}^i - t_{tj})^2 / 2)$$

In these expressions, $P(0)$ is the number of primary ions per unit time produced at the electron beam, which need not be determined since it occurs identically in each case. K_i is the proportionality constant between the amount of time an ion has been in the observing field and the instantaneous power absorption.^{1,5} To compare different ions, we need only observe that $K_i \propto 1/m_i$, where m_i is the mass of the ion. N is the number density of neutral species present. The sum of the rate constants of all reactions causing depletion of the primary ion is denoted by I , while the corresponding quantity for a secondary species i is denoted as J_i . The length of time that an ion spends in passing through the source region and the total cell are, respectively, t_i and t_i^i .

*Note that this equation has been given incorrectly in reference (4); the remainder of the analysis found therein is, however, correct.

The above expressions form the basis for the computer program found in Appendix I. Simplified equations were used to provide approximate rate constants. Predicted intensities derived on the basis of those rate constants were compared to observed intensities, and the rate constants modified accordingly. Agreement to a factor of ten better than the accuracy of experimentally measured intensities was obtained in a modest number of iterations.

As a test of this analysis, the well studied reaction



was examined.⁷ Recent work⁸ in other systems indicates a value of 12×10^{-10} cc molecule⁻¹ sec⁻¹ for the rate constant of this reaction, although widely varying values have been reported.¹ The method described above was used to extract this rate constant from ICR intensity vs. pressure data, with the results seen in Table II-1. The decrease in calculated reaction rate with pressure as predicted by Comisarow⁵ is seen, although any extrapolation to zero pressure is precluded by large experimental scatter.

Even if multiple determinations were used to reduce such scatter, however, a more serious limitation is present. Rate constants in expressions (1) to (3) always appear in the form Nkt , and thus they cannot be determined with greater accuracy than can the ion residence times. By using a square-wave pulsing of the cell trapping voltage, it is possible to get an experimental measure of these times.⁷ This is done by shortening the time between ion ejections, and determining

⁷The author is indebted to Dr. J.L. Beauchamp who carried out these experiments.

⁸S.K. Gupta, E.G. Jones, A.G. Harrison, and J.I. Myher, Can. J. Chem. 45, 3107 (1967).

Table II-1: RATE CONSTANTS FOR THE REACTION



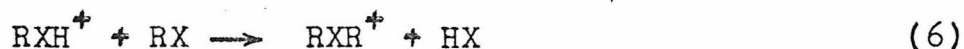
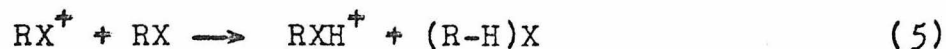
Pressure (Torr x 10 ⁵)	Rate Constant (cc molecule ⁻¹ sec ⁻¹ x 10 ¹⁰)
0.42	10.91
0.58	8.93
0.79	9.76
1.00	9.02
1.02	8.82
1.18	8.22
1.41	8.81
1.75	8.35
2.31	8.22
2.98	7.92

the cutoff point at which ions no longer have enough time between pulses to reach the electrometer at the end of the cell. Residence times measured in this way are between 14 and 44% shorter than calculated times, while refinements in the calculations⁶ actually give longer times. Furthermore, the difference between theory and experiment is a function of magnetic field strength⁷, and will thus vary for ions of differing mass when the conventional field sweep mode is employed. At the present time, the discrepancies are such that it is not immediately clear whether the calculations or the measurements are in error.

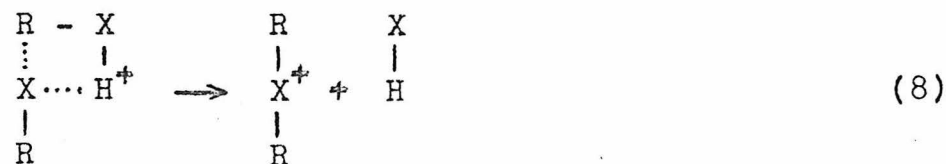
Despite this major obstacle, the value of 8.98×10^{-10} cc molecule⁻¹ sec⁻¹ obtained by averaging all determinations is not far from the accepted value. The use of experimentally measured residence times would raise this value to 10.80×10^{-10} cc molecule⁻¹ sec⁻¹, and a rough extrapolation to zero pressure would yield an even higher value. One expects on the basis of this study, then, that ICR may be used to obtain approximate values for reaction rates, while the cancellation of systematic error might provide even better results for relative rates.

B. Reactions of the Alkyl Halides

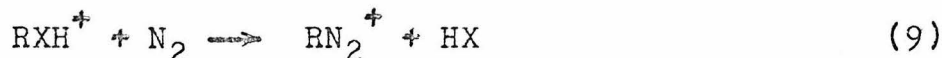
The alkyl halides exhibit an exceedingly rich ion chemistry.^{1,9} In this study three important reactions will be considered in detail:



In methyl and ethyl fluoride and chloride, reaction (5) is the major initial reaction of the species RX^+ , probably proceeding through a combination of proton transfer and hydrogen atom abstraction. At higher pressures, the RXH^+ ion formed in (5) reacts to give RXR^+ , eliminating HX . The mechanism of this reaction has been well studied,⁹ and has been shown to consist primarily of nucleophilic attack by the neutral species:



The formation of the temporary bond to hydrogen is probably of great importance in causing this reaction to proceed efficiently. Such displacement reactions can be made to occur with other neutrals than RX . In cases where the neutral is non-polar and has a low proton affinity, such as



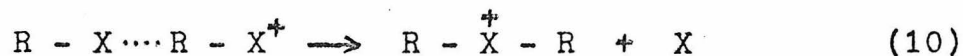
the reaction is considerably slower¹⁰, which may be attributed to the lower propensity for hydrogen bond formation. Additional

⁹D. Holtz, S.L. Patt, and J.L. Beauchamp, to be published.

¹⁰D. Holtz, unpublished data.

support for the proposed mechanism is provided by observations of reactions between mixed species, i.e., RXH^+ and $\text{R}'\text{X}$. It is found that if $\text{PA}(\text{R}'\text{X}) > \text{PA}(\text{RX})$, then simple proton transfer and not displacement will occur, suggesting the importance of the intermediate seen in (8).

For methyl and ethyl bromide and iodide, reaction (5) is an endothermic process, and (7) is thus the only reaction channel open to the RX^+ ion. The RXR^+ ion is thus formed directly, presumably again by nucleophilic attack,



although the hydrogen bond of (8) can no longer be formed.

Typical studies of ion abundance (mass corrected) vs. pressure for the alkyl halides are seen in Figures II-1 through II-5¹¹. Figure II-3, for example, illustrates the ion chemistry of ethyl chloride. Reactions (5) and (6) are in clear evidence, as are the reactions of C_2H_4^+ , the only other primary ion at 12.5 eV. This ion reacts with the parent molecule by extracting H_2^- across the C-C bond, yielding $\text{CH}_2=\text{CHCl}^+$, and in lesser amounts to give the condensation products C_4H_9^+ and C_4H_8^+ .

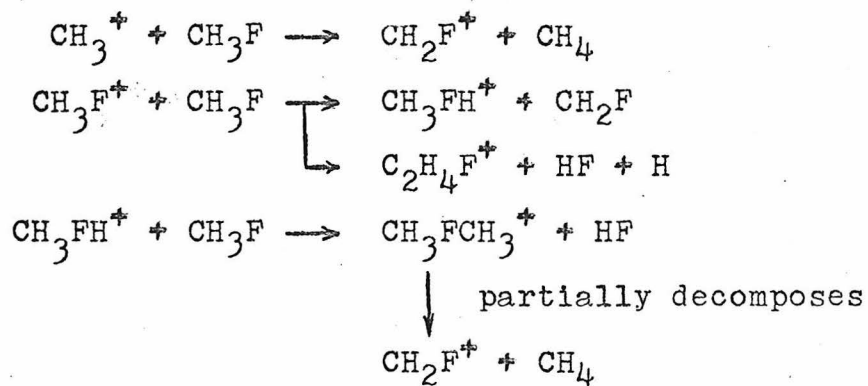
The extremely simple chemistry of $\text{C}_2\text{H}_5\text{Br}$ at 12.0 eV is shown in Figure II-4. At 70.0 eV (Figure II-5), one finds the additional primary ions C_2H_3^+ and C_2H_5^+ . Since both C_2H_2 and C_2H_4 have lower proton affinities than that of $\text{C}_2\text{H}_5\text{Br}$ ¹², proton transfer to $\text{C}_2\text{H}_5\text{Br}$ will occur from both

¹¹The author acknowledges the experimental work on the alkyl halides done by Drs. J.L. Beauchamp, D. Holtz, and S. Sample.

¹²J.L. Franklin *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26 (U.S. Government Printing Office, Washington, D.C.)

Figure II-1:

CH_3F studied at electron energy = 70.0 V. The reaction scheme is



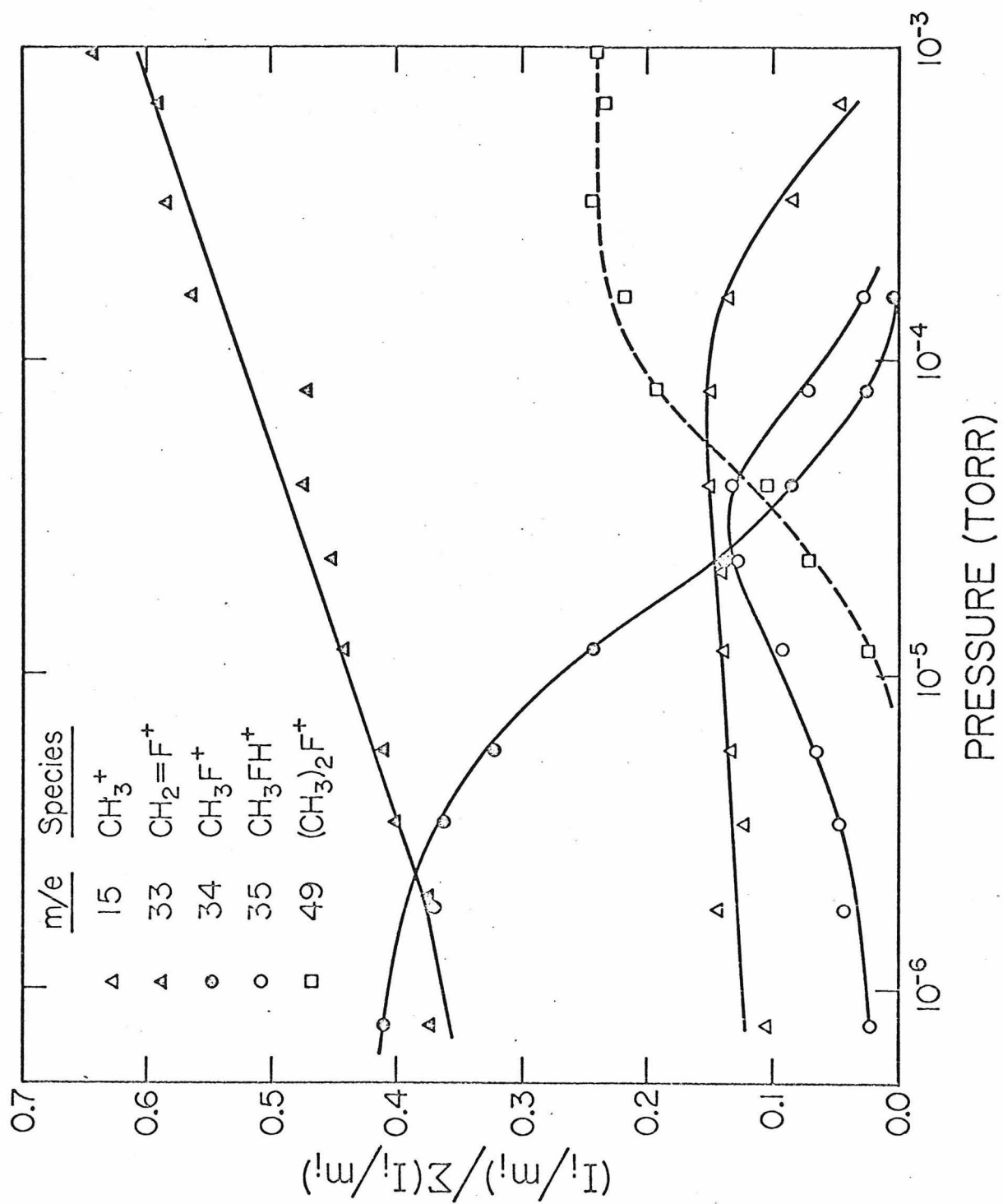
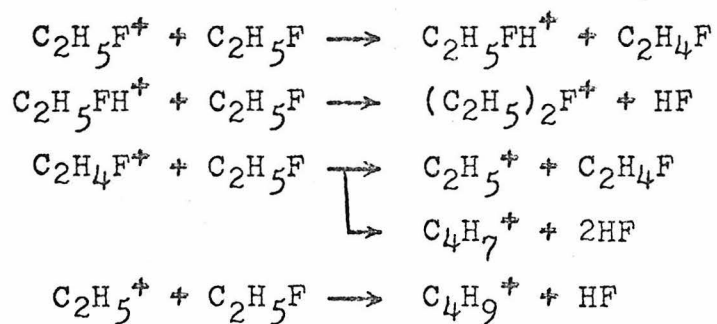


Figure II-2:

$\text{C}_2\text{H}_5\text{F}^+$ studied at electron energy = 13.4 eV. The reaction scheme is



($\text{C}_3\text{H}_6\text{F}^+$ is generated in several reaction sequences involving minor intermediates not shown in this figure.)

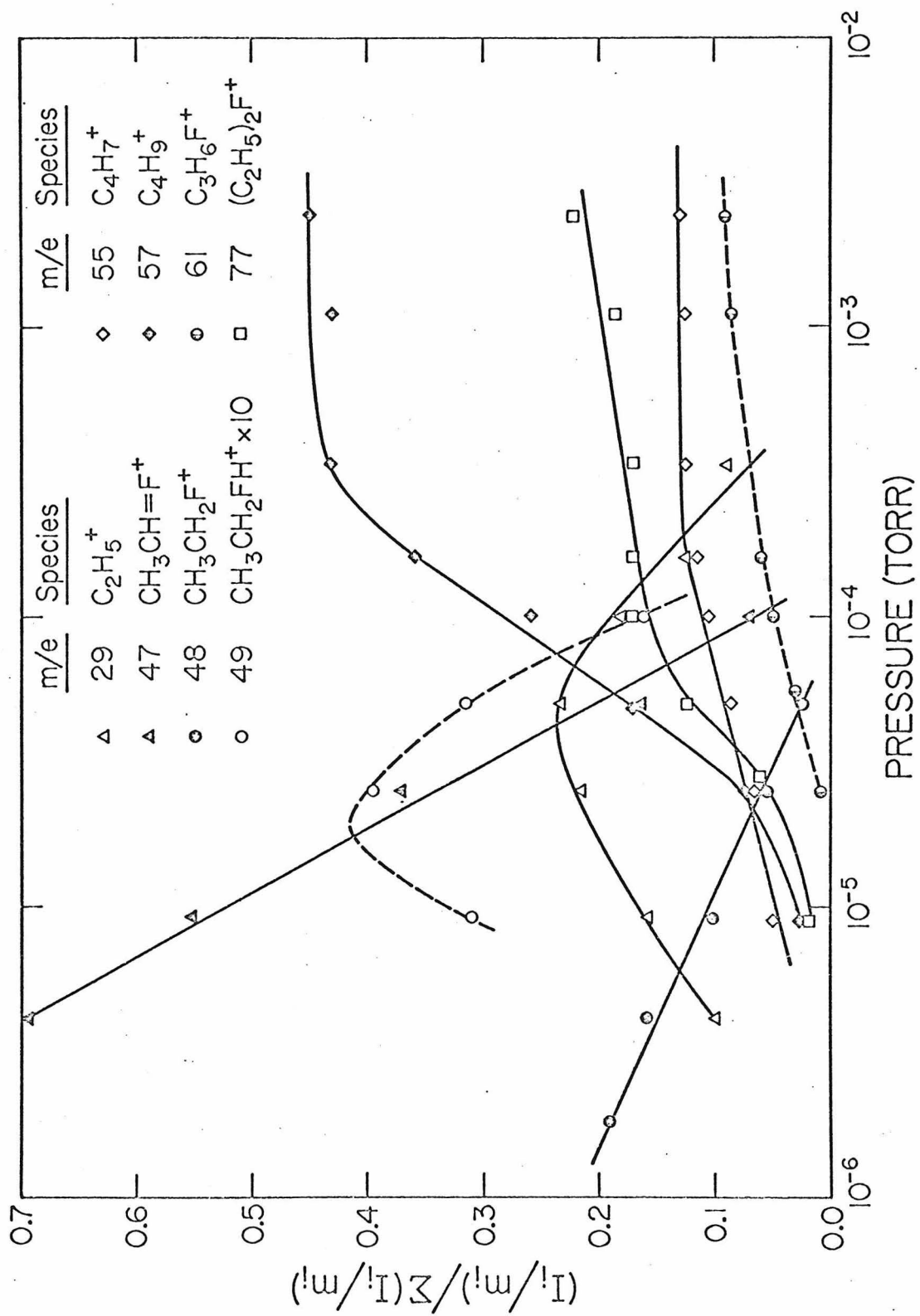
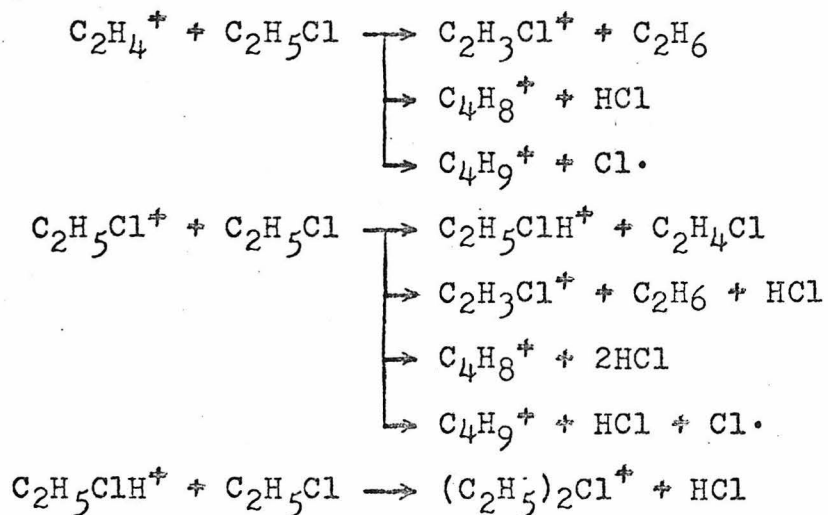


Figure II-3:

C_2H_5Cl studied at electron energy = 12.5 V. The reaction scheme is



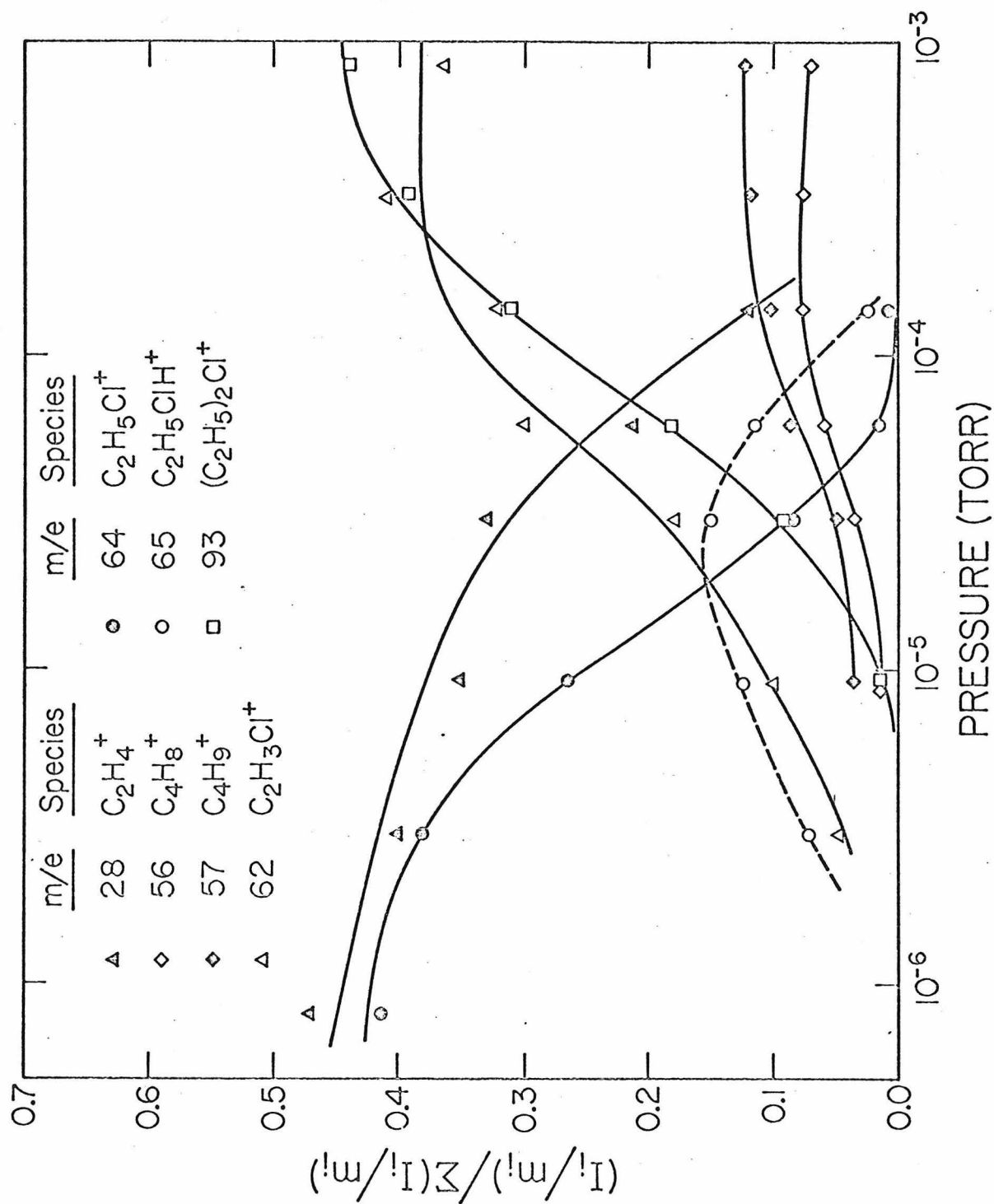


Figure II-4:

$\text{C}_2\text{H}_5\text{Br}$ studied at electron energy = 12.0 V. The reaction scheme is



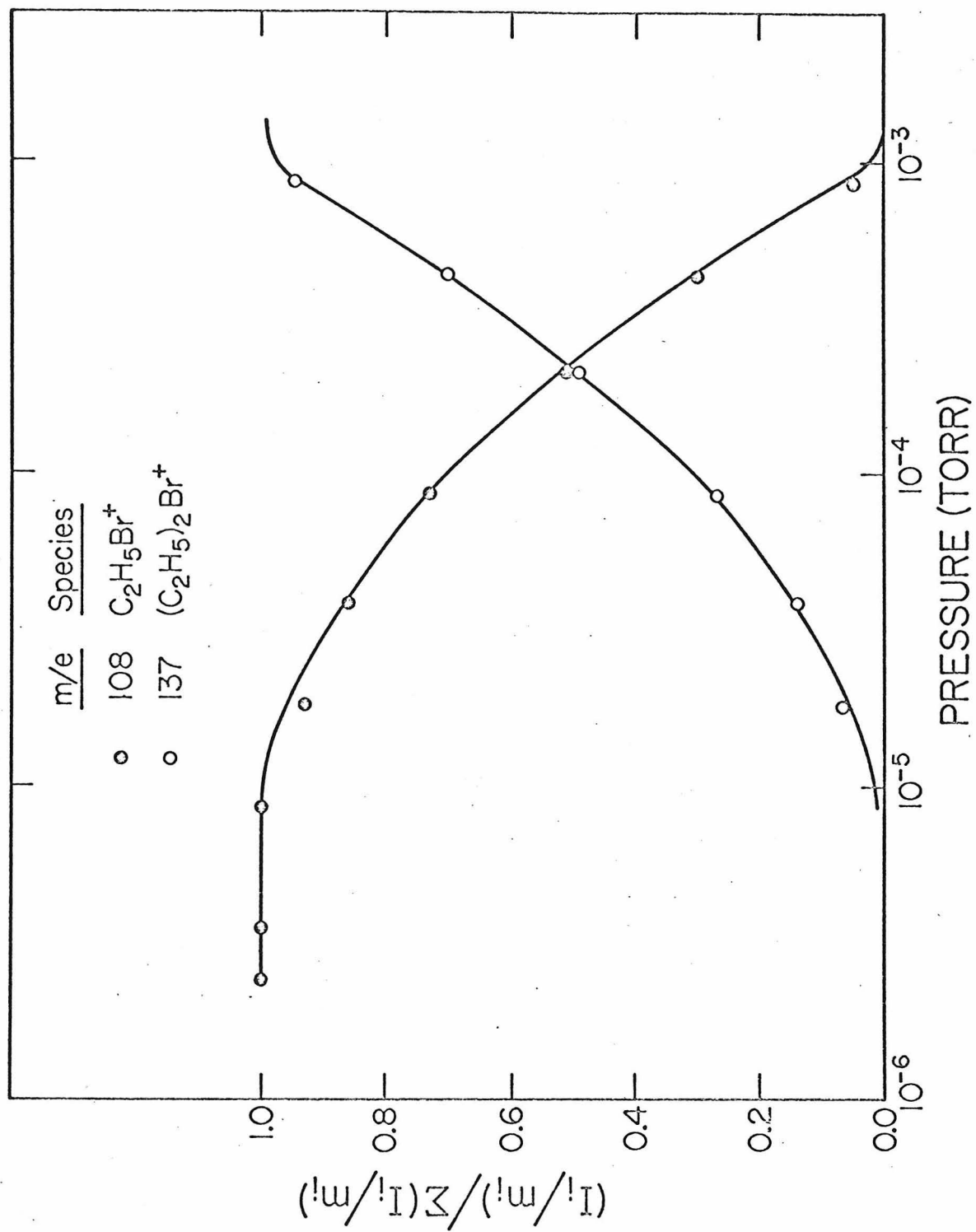
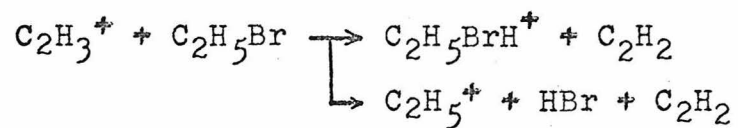
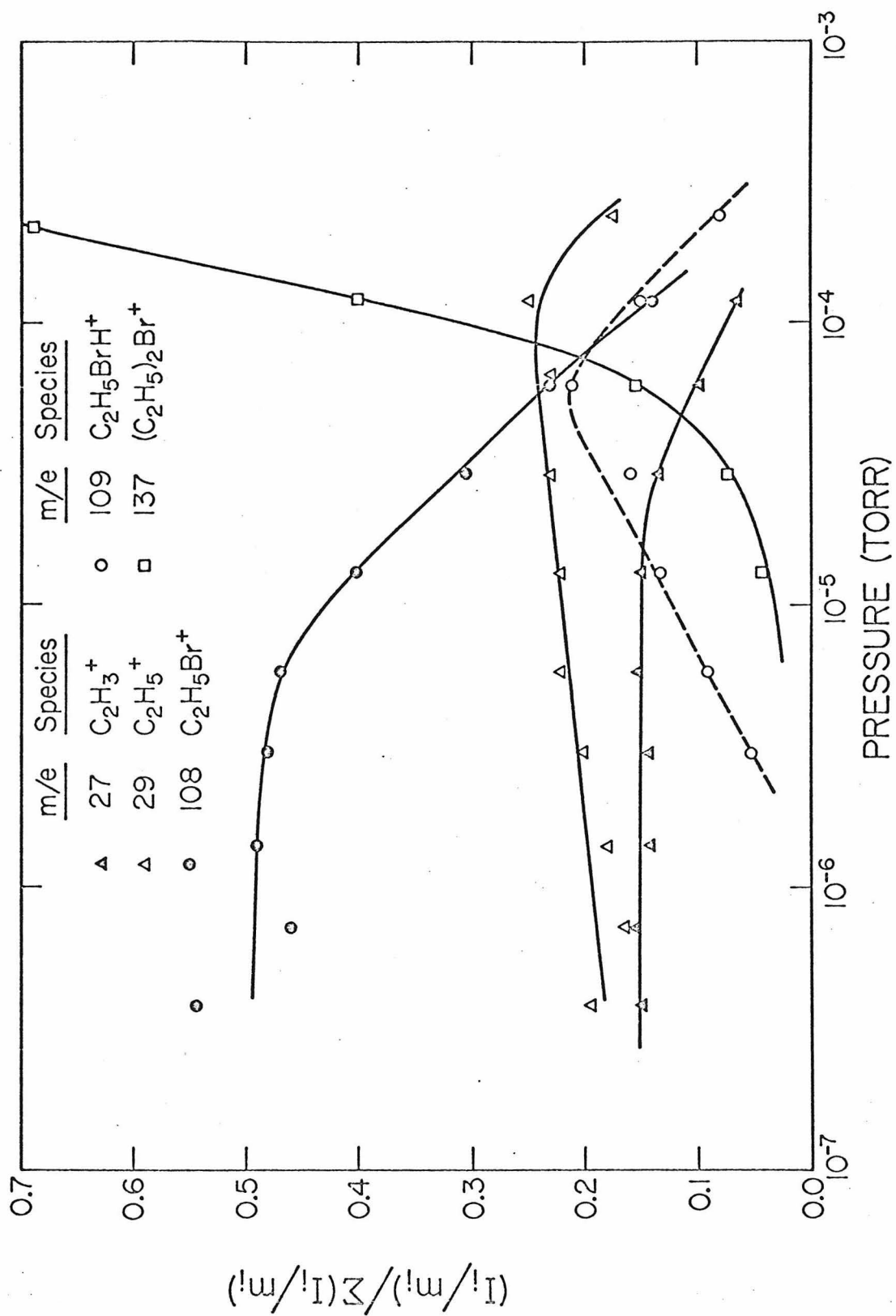


Figure II-5:

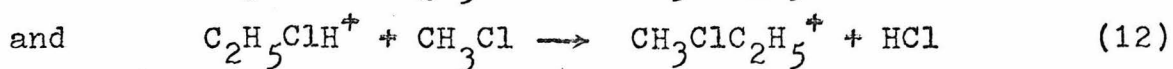
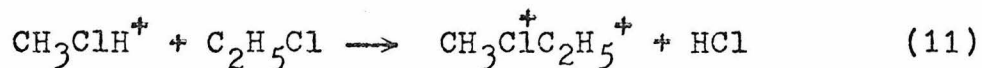
$\text{C}_2\text{H}_5\text{Br}$ studied at electron energy = 70.0 V. The reaction scheme is





$C_2H_3^+$ and $C_2H_5^+$. The $C_2H_5BrH^+$ generated in this manner may then react as in (6) to provide an additional source of the diethylbromonium ion, and qualitatively the latter does indeed seem to form faster than it does at 12.0 eV.

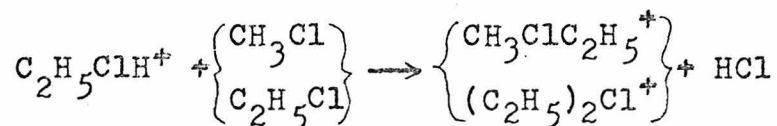
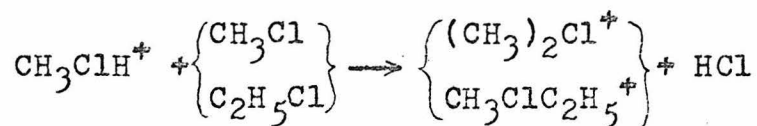
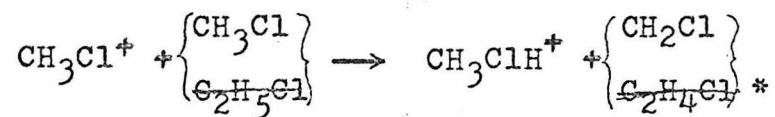
A study of a mixture of methyl and ethyl chlorides (3.5:1) at 70.0 eV is seen in Figure I-6. The interesting thing here is the formation of the methylethylchloronium ion. Double resonance studies indicate that both



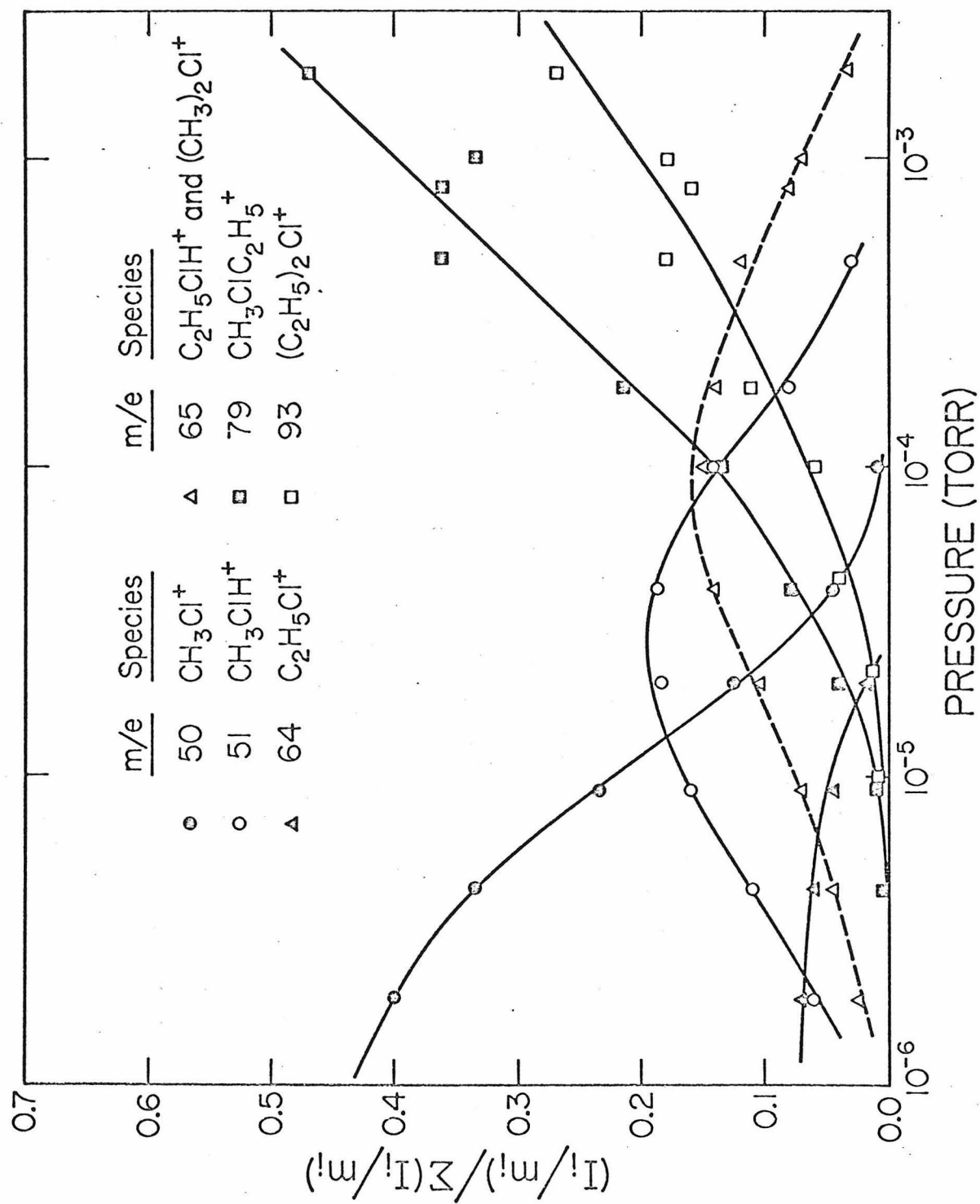
are taking place, but that the chlorine atom in the product ion invariably originates in the methyl chloride species, be it neutral parent or protonated ion. This is readily explained with the reaction mechanism of (8) above, along with the observation⁹ that $PA(C_2H_5Cl) > PA(CH_3Cl)$. One can think of (11), then, as proton transfer followed immediately by nucleophilic attack by the CH_3Cl , before the complex has time to fall apart.

Figure II-6:

A 3:1 mixture of CH_3Cl and $\text{C}_2\text{H}_5\text{Cl}$ studied at electron energy = 70.0 V. The reaction scheme is:



*This reaction is endothermic by 4 kcal/mole.



C. Rates of the Alkyl Halide Reactions

There are two basic treatments which may be considered for the theoretical calculation of ion-molecule reaction rates. Gioumousis and Stevenson¹³ considered the ion-induced dipole interaction, and found

$$k_{G-S} = 2\pi e(\alpha/\mu)^{\frac{1}{2}} \quad (13)$$

where e is the electronic charge, α is the polarizability of the neutral molecule, and μ is the reduced mass of the reaction pair. If the presence of a permanent dipole in the neutral species causes a "locking-in" as the ion approaches, one must add an additional term to account for this, and the resulting expression for the locked dipole model (L-D) is^{8,14}

$$\begin{aligned} k &= k_{G-S} + (2\pi e\mu_0)(2/\mu\pi kT)^{\frac{1}{2}} \quad (14) \\ &= k_{G-S} + k_{L-D} \end{aligned}$$

In this expression, μ_0 is the permanent dipole moment of the neutral, k is Boltzman's constant and T is the temperature. We note that unlike the G-S model, this model predicts a temperature dependent rate constant, or equivalently an ion velocity dependent rate.

The ion-molecule reactions of the alkyl halides, the experimentally determined rate constants, k_{G-S} and k_{L-D} are listed in Table II-2. The first conclusion that may be drawn is that the locked dipole model seems to inaccurately represent these reactions, while the

¹³G. Gioumousis and D.P. Stevenson, J. Chem. Phys. 29, 294 (1958).

¹⁴R. A. Fluegge, J. Chem. Phys. 50, 4373 (1969).

Table II-2. RATE CONSTANTS FOR THE REACTIONS OF THE ALKYL HALIDES

Reaction	Experimental	k _{G-S}	k _{L-D}
CH ₃ F ⁺ + CH ₃ F → CH ₃ FH ⁺ + CH ₂ F ⁺	k ₁ = 12.8	Σ = } 9.10	40.44
CH ₃ F ⁺ + CH ₃ F → C ₂ H ₄ F ⁺ + HF + H	k ₂ = 0.96		
CH ₃ FH ⁺ + CH ₃ F → (CH ₃) ₂ F ⁺ + HF	k ₃ = 7.1	9.04	40.15
C ₂ H ₅ F ⁺ + C ₂ H ₅ F → C ₂ H ₅ FH ⁺ + C ₂ H ₄ F ⁺	k ₄ = 15.0		
C ₂ H ₅ FH ⁺ + C ₂ H ₅ F → (C ₂ H ₅)F ⁺ + HF	k ₅ = 14.0		
CH ₃ Cl ⁺ + CH ₃ Cl → CH ₃ ClH ⁺ + CH ₂ Cl ⁺	k ₆ = 12.5	9.87	35.74
CH ₃ ClH ⁺ + CH ₃ Cl → (CH ₃) ₂ Cl ⁺ + HCl	k ₇ = 1.4	9.82	35.74
C ₂ H ₅ Cl ⁺ + C ₂ H ₅ Cl → C ₂ H ₅ ClH ⁺ + C ₂ H ₄ Cl ⁺	k ₈ = 9.4	Σ = } 10.39	33.22
C ₂ H ₅ Cl ⁺ + C ₂ H ₅ Cl → C ₂ H ₃ Cl ⁺ + C ₂ H ₆ + HCl	k ₉ = 4.0		
C ₂ H ₅ Cl ⁺ + C ₂ H ₅ Cl → C ₄ H ₈ ⁺ + 2HCl	k ₁₀ = 0.70		
C ₂ H ₅ Cl ⁺ + C ₂ H ₅ Cl → C ₄ H ₉ ⁺ + HCl + Cl•	k ₁₁ = 0.85	Σ = } 12.60	40.30
C ₂ H ₄ ⁺ + C ₂ H ₅ Cl → C ₄ H ₈ ⁺ + HCl	k ₁₂ = 0.83		
C ₂ H ₄ ⁺ + C ₂ H ₅ Cl → C ₄ H ₉ ⁺ + Cl•	k ₁₃ = 1.24		
C ₂ H ₄ ⁺ + C ₂ H ₅ Cl → C ₂ H ₃ Cl ⁺ + C ₂ H ₆	k ₁₄ = 2.71		
C ₂ H ₄ ⁺ + C ₂ H ₅ Cl → C ₂ H ₄ Cl ⁺ + C ₂ H ₅	k ₁₅ = 0.47		
C ₂ H ₅ ClH ⁺ + C ₂ H ₅ Cl → (C ₂ H ₅) ₂ Cl ⁺ + HCl	k ₁₆ = 5.5	10.35	33.10
CH ₃ Br ⁺ + CH ₃ Br → (CH ₃) ₂ Br ⁺ + Br•	k ₁₇ = 0.55	7.93	23.93
C ₂ H ₅ Br ⁺ + C ₂ H ₅ Br → (C ₂ H ₅) ₂ Br ⁺ + Br•	k ₁₈ = 0.56	8.55	24.97
CH ₃ I ⁺ + CH ₃ I → (CH ₃) ₂ I ⁺ + I•	k ₁₉ = 0.055	7.50	17.93
C ₂ H ₅ I ⁺ + C ₂ H ₅ I → (C ₂ H ₅) ₂ I ⁺ + I•	k ₂₀ = 0.16	7.97	19.76

Table II-3. Polarizabilities and Dipole Moments
of the Alkyl Halides

Species	Polarizability ^a (A ³)	Dipole Moment ^b (Debye)
CH ₃ F	2.57	1.81
C ₂ H ₅ F		1.95
CH ₃ Cl	4.44	1.94
C ₂ H ₅ Cl	6.30	2.04
CH ₃ Br	5.44	1.79
C ₂ H ₅ Br	7.33	2.01
CH ₃ I	7.29	1.64
C ₂ H ₅ I		1.90

^aE.W. Rothe and R.B. Bernstein, J. Chem. Phys. 31, 1619 (1959)

^bA.L. McClellan, "Tables of Experimental Dipole Moments,"
W.H. Freeman and Co., San Francisco, 1963.

Table II-4. Thermochemical Data of the Alkyl Halides

Species (M)	IP(M) ^a eV	PA(M) ^b kcal/mole	HA(M) ^b
CH ₃ F	12.85	147	129
C ₂ H ₅ F	12.00	163	127
CH ₃ Cl	11.22	160	107
C ₂ H ₅ Cl	10.97	168	108
CH ₃ Br	10.53	163	93
C ₂ H ₅ Br	10.29	170	93
CH ₃ I	9.54	170	77
C ₂ H ₅ I	9.33	175	77

^aJ.L. Franklin *et al.*, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26 (U.S. Government Printing Office, Washington, D.C., 1969).

^bD. Holtz, S. Sample, S. Patt, and J.L. Beauchamp, to be published.

Gioumousis-Stevenson ion-induced dipole model seems to be a much better first approximation to reality.

One must bear in mind that expression (13) is derived on the assumption that all collisions will be reactive. Clearly, this is not necessarily the case, and one might expect that a simple proton transfer or hydrogen atom abstraction reaction such as (5) is likely to occur far more efficiently than a more complex condensation reaction such as (7), where more intimate contact between ion and neutral is required. On this basis, one can understand the extreme slowness of Reactions 17 through 20 in Table II-2.

When one considers the total reactivity of the parent ions CH_3F^+ , $\text{C}_2\text{H}_5\text{F}^+$, CH_3Cl^+ , and $\text{C}_2\text{H}_5\text{Cl}^+$, one finds values of 13.8, 15.0, 12.5, and 15.0 cc molecule⁻¹ sec⁻¹, respectively. All of these are equally similar to the rate predicted by the G-S model. Considering the rates for the corresponding protonated species, however, one finds values of 7.1, 14.0, 1.4, and 5.5 cc molecule⁻¹ sec⁻¹, respectively. It is not completely clear what effects these values represent. The $(\text{CH}_3)_2\text{F}^+$ ion can partially decompose to give $\text{CH}_2\text{F}^+ + \text{CH}_4$ and thus k_3 as formally written may actually be higher than 7.1. No such decomposition, however, is observed in the chloride species.

It seems reasonable to believe that at least some of the effects seen have steric origin. One certainly would expect reaction 17 through 20 to proceed through an identical mechanism, and the factor of 5 to 10 difference in the rate constants for the bromine species

and the iodine species seems to indicate such steric effects.

D. Conclusions

The reactions of the alkyl halides have been studied and rate constants for appropriate reactions determined. Only a limited number of these have been previously reported. Marshall and Buttrill⁴ found $k_1 = 13.6$, $k_2 = 0.96$, and $k_3 = 8.0$ (all cc molecule⁻¹ sec⁻¹ x 10⁻¹⁰), in good agreement with the values reported here. Values for k_6 have been reported as 12.1⁸, 19.4¹⁵, and 18.8¹⁶, again in reasonable agreement, while k_8 has been reported as 26.8¹⁷.

The determination of reaction rates in mass spectrometric studies is complicated by the dependence of these rates on repeller field strength. Despite the difficulties discussed above with respect to the drift times, ICR seems to be a valuable addition in the measurement of reaction rates. The studies reported in this work were limited to the simple treatment of Marshall and Buttrill described above. A further extension of this method to such cases as two different reactants producing one product is feasible and would add a great deal to the capabilities of the method.

¹⁵N.A. McAskill, Australian J. Chem. 22, 2275 (1969)

¹⁶A.G. Harrison and J. Thynne, Adv. Chem. Ser. 58, 150 (1968).

¹⁷T.O. Tiernan and M. Hughes, Adv. Chem. Ser. 82, 412 (1968).

APPENDIX I

C

DIMENSION DENS(20),SIZED(20,20),MASS(20),NPREC(20),TAU(20),
C TAUP(20),RATE(20,20,20),RATEI(20,20),RATEJ(20,20),
C SIZE(20,20),FACT(20),NCON(20)

C

C INPUT CELL DIMENSIONS, G/AMU, DRIFT VOLTAGES, NUMBER OF SPECTRA
READ (5,101) D, ALEN1, ALEN2

31 READ (5,102) GAMU,VSOOR,VRES,NSPEC
IF (GAMU.EQ.0.) GO TO 30

C

C INPUT SPECTRUM CARDS - NUMBER, PRESSURE, INTENSITIES

1 CONTINUE

READ (5,103) NUMBER,DENS(NUMBER),NPEAKS,(SIZED(I,NUMBER),

C I=1,NPEAKS)

IF (DENS(NUMBER).LT.1.) DENS(NUMBER)=DENS(NUMBER)*3.23E16

IF (NUMBER.NE.NSPEC) GO TO 1

C

C INPUT NUMBER OF EACH TYPE OF ION , ION MASSES, AND PRECURSORS
READ (5,104) NPRIM,NSEC,NTERT, (MASS(I),I=1,NPEAKS),

C (NPREC(I),I=1,NPEAKS)

NPRIMP=NPRIM+1

NSECP=NSEC+1

C

C CALCULATE TAU AND TAU-PRIME FOR EACH ION

DO 2 I=1,NPEAKS

TAU(I)=ALEN1*GAMU*MASS(I)*D/(VSOOR*10**8)

TAUP(I)=TAU(I)+ALEN2*GAMU*MASS(I)*D/(VRES*10**8)

WRITE (6,112) GAMU,VSOOR,VRES,TAU(1),TAUP(1)

C

C REPEAT WHOLE PROGRAM ONCE FOR EACH SPECTRUM

DO 22 NUMBER=1,NSPEC

NCON(NUMBER)=1

C

C CALCULATE INITIAL RATE CONSTANTS

3 DO 4 J=NPRIMP,NTERT

DO 40 I=1,NPEAKS

40 RATE(I,J,NUMBER)=0

B5=TAU(NPREC(J))+TAUP(NPREC(J))

RATE(NPREC(J),J,NUMBER)=2*MASS(NPREC(J))*SIZED(J,NUMBER)/

C (DENS(NUMBER)*B5*(MASS(NPREC(J))*SIZED(J,NUMBER)+

C MASS(J)*SIZED(NPREC(J),NUMBER)))

IF (NUMBER.NE.1) RATE(NPREC(J),J,NUMBER)=RATE(NPREC(J),J,NUMBER-1)

4

CONTINUE

C

C INITIALIZE ITERATION COUNTER

ITER=1

C

C CALCULATE BUTTRILL'S I AND J-SUB-I

23 DO 5 I=1,NPRIM

RATEI(I,NUMBER)=0

DO 5 J=NPRIMP,NSEC

5

RATEI(I,NUMBER)=RATEI(I,NUMBER)+RATE(I,J,NUMBER)

C

C NORMALIZE OBSERVED INTENSITIES

DO 19 N=1,NPRIM

SUM2=0

```
DO 18 IB=1,NPEAKS
IF (NPREC(IB).EQ.N.OR.NPREC(NPREC(IB)).EQ.N) SUM2=SUM2+SIZEO(IB,
C NUMBER)
18 CONTINUE
DO 19 IB=1,NPEAKS
IF (NPREC(IB).EQ.N.OR.NPREC(NPREC(IB)).EQ.N) SIZEO(IB,NUMBER)=
C SIZEO(IB,NUMBER)/SUM2
19 CONTINUE
C
C BRANCH IF NO TERTIARIES
IF (NTERT.EQ.NSEC) GO TO 7
DO 6 J=NPRIMP,NSEC
RATEJ(J,NUMBER)=0
DO 6 K=NSECP,NTERT
6 RATEJ(J,NUMBER)=RATEJ(J,NUMBER)+RATE(J,K,NUMBER)
C
C CALCULATE PREDICTED INTENSITIES
7 DO 8 I=1,NPRIM
A1=DENS(NUMBER)*RATEI(I,NUMBER)
C
C BUTTRILL'S EQUATION (19)
C
8 SIZE(I,NUMBER)=(EXP(-A1*TAU(I))-EXP(-A1*TAUP(I))-A1*(TAUP(I)-
C TAU(I))*EXP(-A1*TAUP(I)))/(MASS(I)*RATEI(I,NUMBER))
C
DO 9 J=NPRIMP,NSEC
A2=DENS(NUMBER)
A3=TAU(J)
A4=TAUP(J)
A5=RATEI(NPREC(J),NUMBER)
C
C BRANCH IF NO TERTIARIES
IF (NTERT.EQ.NSEC) GO TO 24
NCHECK=0
DO 51 K=NSECP,NTERT
IF (NPREC(K).EQ.J) NCHECK=1
51 CONTINUE
IF (NCHECK.EQ.0) GO TO 24
A6=RATEJ(J,NUMBER)
C
C BUTTRILL'S EQUATION (25)
C
SIZE(J,NUMBER)=(RATE(NPREC(J),J,NUMBER)*EXP(-A2*A5*A3)/(MASS(J)*
C A6**2*(A5-A6)**2))*(A5**2+A5*A6*EXP(-A2*A6*(A4-A3))-A6**2*
C EXP(-A2*A5*(A4-A3))+A5*(A5-A6)*EXP(-A2*(A6-A5)*A3)-A5*(A5-A6)*
C (1+A2*A6*(A4-A3))*EXP(-A2*A6*A4+A2*A5*A3)-A5*A6)
C
IF (SIZE(J,NUMBER).LT.0.) SIZE(J,NUMBER)=SIZE(J,NUMBER)*(-1)
GO TO 9
24 SIZE(J,NUMBER)=RATE(NPREC(J),J,NUMBER)/(MASS(J)*A5**2)*((A2**2*A5
C **2*(A4-A3)**2/2-A2*A5*(A4-A3)*EXP(-A2*A5*A3)+EXP(-A2*A5*A3)-
C EXP(-A2*A5*A4))
9 CONTINUE
C
C BRANCH IF NO TERTIARIES
IF (NTERT.EQ.NSEC) GO TO 11
```

```

DO 10 K=NSECP,NTERT
A7=RATE(NPREC(NPREC(K)),NPREC(K),NUMBER)
A8=RATE(NPREC(K),K,NUMBER)
A9=RATEI(NPREC(NPREC(K)),NUMBER)
B1=RATEJ(NPREC(K),NUMBER)
B2=TAU(K)
B3=TAUP(K)
B4=B3-B2

```

C

C BUTTRILL'S EQUATION (31)

C

```

10 SIZE(K,NUMBER)=A7*A8/(MASS(K)*A9*B1**3*(A9-B1))*((A9**3-A2*A9**3
C *B1*B4)*EXP(-A2*B1*B2)-(B1**3-A2*B1**3*A9*B4)*EXP(-A2*A9*B2)+
C B1**3*EXP(-A2*A9*B3)-A9**3*EXP(-A2*B1*B3)+A2**2*A9**2*B1**2*(A9-
C B1)*B4**2/2)/A9

```

C

C NORMALIZE CALCULATED INTENSITIES

11

DO 16 N=1,NPRIM

SUM1=0

DO 17 IA=1,NPEAKS

```

IF(NPREC(IA).EQ.N.OR.NPREC(NPREC(IA)).EQ.N) SUM1=SUM1+SIZE(IA,
C NUMBER)

```

17

CONTINUE

DO 16 IA=1,NPEAKS

```

IF (NPREC(IA).EQ.N.OR.NPREC(NPREC(IA)).EQ.N) SIZE(IA,NUMBER)=
C SIZE(IA,NUMBER)/SUM1

```

16

CONTINUE

14

WRITE (6,120)

WRITE (6,105) (SIZE(I,NUMBER),I=1,NPEAKS)

15

WRITE (6,105) (SIZE(I,NUMBER),I=1,NPEAKS)

DO 20 J=NPRIMP,NTERT

20

WRITE(6,106) MASS(NPREC(J)),MASS(J),NUMBER,RATE(NPREC(J),J,NUMBER)

C

C COMPARE CALCULATED INTENSITIES TO OBSERVED ONES AND CORRECT RATE CONSTANTS

IF (NSEC.EQ.NTERT) GO TO 32

DO 12 J=NSECP,NTERT

FACT(J)=SIZE(J,NUMBER)*SIZE(NPREC(J),NUMBER)/(SIZE(J,NUMBER)*

C SIZE(NPREC(J),NUMBER))

FACT(J)=SQRT(ABS(FACT(J)))

IF (FACT(J).GT.2.) FACT(J)=2.

IF (FACT(J).LT.0.5) FACT(J)=0.5

RATE(NPREC(J),J,NUMBER)=RATE(NPREC(J),J,NUMBER)*FACT(J)

12

CONTINUE

32

DO 13 J=NPRIMP,NSEC

IF (SIZE(NPREC(J),NUMBER).EQ.0.) SIZE(NPREC(J),NUMBER)=

C SIZE(NPREC(J),NUMBER)

IF (SIZE(NPREC(J),NUMBER).EQ.0.) GO TO 13

FACTP=1

DO 60 K=NSECP,NTERT

IF (NPREC(K).EQ.J) FACTP=SIZE(K,NUMBER)/SIZE(J,NUMBER)

60

CONTINUE

```

FACT(J)=(SIZE(J,NUMBER)/SIZE(J,NUMBER))**2*FACTP*SIZE(NPREC(J),
C NUMBER)/SIZE(NPREC(J),NUMBER)

```

AFACT=ABS(FACT(J))

IF (AFACT.GT.4.) FACT(J)=4.

IF (AFACT.LT.0.25) FACT(J)=0.25

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```

    RATE(NPREC(J),J,NUMBER)=RATE(NPREC(J),J,NUMBER)/SQRT(ABS(FACT(J)))
13  CONTINUE
C
C IF ITERATIONS EXCEED 30, PROCEED TO NEXT RUN
    IF (ITER.EQ.30) GO TO 25
    ITER=ITER+1
C
C IF CONVERGENCE HAS OCCURED, PROCEED TO NEXT RUN
    DO 21 I=1,NPEAKS
      B6=ABS(SIZE(I,NUMBER)-SIZEO(I,NUMBER))
      IF (SIZEO(I,NUMBER).EQ.0.) GO TO 21
      IF (B6.GT.1.E-4) GO TO 23
21  CONTINUE
      GO TO 26
25  WRITE (6,107)
      NCON(NUMBER)=2
      GO TO 27
26  WRITE (6,108)
27  WRITE (6,110)
22  CONTINUE
80  DO 81 NUMBER=1,NSPEC
81  DENS(NUMBER)=DENS(NUMBER)/(3.23E16)
      DO 28 J=NPRIMP,NTERT
        WRITE (6,109) MASS(NPREC(J)),MASS(J)
        WRITE (6,111)
        DO 29 NUMBER=1,NSPEC
          IF (NCON(NUMBER).EQ.1) WRITE (6,113) MASS(NPREC(J)),MASS(J),
C NUMBER,RATE(NPREC(J),J,NUMBER),DENS(NUMBER)
          IF (NCON(NUMBER).EQ.2) WRITE (6,115) MASS(NPREC(J)),MASS(J),
C NUMBER,RATE(NPREC(J),J,NUMBER),DENS(NUMBER)
29  CONTINUE
        WRITE (6,120)
28  CONTINUE
        WRITE (6,110)
        GO TO 31
      STOP
$
01) IEY002I LABEL
30  CONTINUE
C
101  FORMAT (F4.2,2F5.2)
102  FORMAT (F5.1,2F5.2,13)
103  FORMAT (I2,E9.2,I3,11F6.2/(13F6.2/))
104  FORMAT (I2,26I3/(26I3/))
105  FORMAT (' ',15F8.4)
106  FORMAT (' K(',I3,',',I3,',',I2,')= ',1PE14.7)
107  FORMAT (' THIS RUN DID NOT CONVERGE')
108  FORMAT (' THIS RUN HAS CONVERGED')
109  FORMAT (' ORATE CONSTANTS FOR (M/E)=',I3,' GOING TO (M/E)=',I3)
110  FORMAT (1H1)
111  FORMAT (1H )
112  FORMAT (' RATES FOR RUNS WITH G/AMU=',F5.1,', V-S=',F5.2,', V-R='
C F5.2,', TAUP=',1PE11.3,', TAUP-PRIME=',E11.3//)
113  FORMAT (' K(',I3,',',I3,',',I2,')=',1PE11.4,10X,'P=',E9.3,
C ' TORR',20X,'CONVERGED')
115  FORMAT (' K(',I3,',',I3,',',I2,')=',1PE11.4,10X,'P=',E9.3,

```

FORTTRAN IV G LEVEL 1, MOD 4

MAIN

DATE =

C ' TORR',20X,'NOT CONVERGED')

0150 120 FORMAT (1H0)

C

0151 END