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REACTIONS OF $C_3H_3^+$ WITH ACETYLENE AND DIACETYLENE IN
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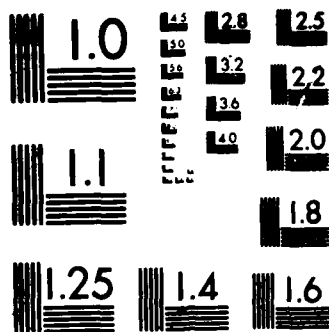
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The reactions of linear $C_3H_3^+$ with acetylene, diacetylene and deuterated acetylene were investigated using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. A rate coefficient of $(1.4 \pm 0.7) \times 10^{-9} \text{ cm}^3/\text{s}$ was obtained for the reaction of linear $C_3H_3^+$ with diacetylene while no production of larger ions was observed with acetylene. Using the ejection capabilities of FTICR, reactions of different $C_3H_3^+$ precursors with C_2H_2 were studied in order to investigate possible production of $C_5H_5^+$ from ionic sources other than $C_3H_3^+$ present in the reaction medium. Linear $C_3H_3^+$ isomerized to the cyclic form in reactions with both acetylene and diacetylene. The isomerization was shown to take place via a long-lived $C_5H_5^+$ complex by isotope exchange reactions between linear $C_3H_3^+$ and deuterated acetylene. Results are discussed in relation to previous work involving $C_3H_3^+$ reactions and a proposed ionic route to soot formation.

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Reactions of $C_3H_3^+$ with Acetylene and Diacetylene in the Gas Phase

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The reactions of linear $C_3H_3^+$ with acetylene, diacetylene, and deuterated acetylene were investigated with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. A rate coefficient of $(1.4 \pm 0.7) \times 10^{-9}$ cm³/s was obtained for the reaction of linear $C_3H_3^+$ with diacetylene while no production of larger ions was observed with acetylene. The ejection capabilities of FTICR were used to study the reactions of different $C_3H_3^+$ precursors with C_2H_2 in order to investigate the possible production of $C_5H_3^+$ from ionic sources other than $C_3H_3^+$ present in the reaction medium. Linear $C_3H_3^+$ isomerized to the cyclic form in reactions with both acetylene and diacetylene. The isomerization was shown to take place via a long-lived $C_3H_3^+$ complex by isotope exchange reactions between linear $C_3H_3^+$ and deuterated acetylene. Results are discussed in relation to previous work involving $C_3H_3^+$ reactions and a proposed ionic route to soot formation.

Introduction

The $C_3H_3^+$ ion has received considerable attention in recent years as a possible soot precursor because it is found in quite high abundance in fuel-rich and sooting flames.¹⁻³ Although substantial uncertainty remains as to $C_3H_3^+$ formation mechanisms in flames,^{4,5} the ion is postulated^{4,6} to react with neutrals such as acetylene, diacetylene, and C_2H in rapid, sequential condensation and condensation/elimination reactions, forming successively larger ions, which can rearrange to cyclic species during the ion/molecule reaction chain.

Michaud et al.³ have made an alternate suggestion that direct reactions of $C_3H_3^+$ with aromatic neutrals such as benzene, toluene, naphthalene, methylnaphthalenes, and indene may be more important in forming polycyclic ions than sequential reactions involving acetylene and diacetylene. In fact, recent ion cyclotron resonance (ICR) studies of reactions of $C_3H_3^+$ with aromatic neutrals showed⁷ that these reactions are fast enough to be considered as possible bypass channels in ionic soot formation pathways in fuel-rich hydrocarbon flames.

Two isomeric structures of $C_3H_3^+$ are important in discussing the role of $C_3H_3^+$ in ion/molecule reaction mechanisms. The first is the cyclopropenyl cation, recognized as the most stable isomer, which has a theoretically calculated heat of formation of 253 kcal/mol,^{8,9} in quite good agreement with the 256 ± 2 kcal/mol determined by experiment.¹⁰ A second and potentially more important $C_3H_3^+$ structure is that of the linear propargylium ion with a calculated^{8,9} heat of formation 31 to 34 kcal/mol higher than that of the cyclopropenyl cation, in fair agreement with the 25 kcal/mol difference found experimentally by Lossing.¹⁰ Recent calculations⁹ have shown several other stable isomeric structures of the $C_3H_3^+$ ion with higher heats of formation relative to the cyclopropenyl cation and propargylium ions.

The importance of different precursors in affecting the reactivity of $C_3H_3^+$ ions was reported in a thermochemical study of Holmes and Lossing.¹¹ In an ICR study of $C_3H_3^+$ reactions, Ausloos and Lias¹² showed that significant fractions of the linear isomer can be produced by charge-transfer reactions of small ions (Ar^+ , Xe^+ , CO^+ , Ne^+ , etc.) with propargyl chloride and bromide. Later it was reported⁷ that even higher proportions of the propargylium isomer relative to the cyclopropenyl cation can be obtained with propargyl iodide either by electron impact or charge exchange using Xe^+ .

A study by Smyth et al.¹³ demonstrated that the cyclopropenyl cation was relatively unreactive toward simple hydrocarbon fuels whereas the linear, propargylium ion was quite reactive. In particular, reaction of propargylium ions with acetylene was reported to produce $C_5H_3^+$ and $C_5H_5^+$ ions with an overall $C_3H_3^+$ disappearance rate coefficient of 1×10^{-9} cm³/s. Since this sequence of reactions is a critical one in the initial stages of the postulated ion/molecule mechanism of soot formation, it was studied as a part of ongoing work¹⁴ in our laboratory related to reactivity and structures of small hydrocarbon ions. Results substantially different from those reported earlier were found and the study was thus expanded to investigate possible production of $C_5H_3^+$ ions from ionic sources other than $C_3H_3^+$ present in the reaction media using the ejection capabilities of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Reactions of propargylium ions with C_2D_2 were also studied in order to delineate further a proposed mechanism for the $C_3H_3^+$ /acetylene interaction.

Diacetylene is another important flame neutral which has been

postulated to react with $C_3H_3^+$ ions in an ion/molecule soot formation mechanism.⁶ Reaction pathways and the rate coefficient for the reaction of propargylium ions with diacetylene near room temperature were thus also investigated. In this paper, results for the reactions of $C_3H_3^+$ ions with acetylene, deuterated acetylene, and diacetylene are reported and discussed in relation to previous work involving $C_3H_3^+$ reactions^{7,12,13} and the proposed^{4,6} ionic route to soot formation.

Experimental Section

A Nicolet FTMS-1000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with a superconducting magnet of fixed magnetic field (3.0 T) was used for the work reported here. Basic principles of the technique and its applications in ion/molecule reaction studies have been reviewed in several recent articles.¹⁵⁻¹⁷ Reaction pathways were delineated by using the ejection capabilities¹⁸ of FTICR which make it possible to eject one ion from a complicated reaction mixture to determine its contribution to the mass spectrum of all the other ions.

Reaction rate coefficients were determined by monitoring the intensity of the $C_3H_3^+$ ions as a function of time (typically at least 2 s) after ejection of all other ions from the analyzer cell. Neutral gas pressures were measured with an ionization gauge. Ionization gauge readings were then corrected by constructing calibration curves of ionization gauge vs. capacitance manometer (MKS-Baratron) readings in the 1×10^{-6} to 1×10^{-4} Torr range. In order to correct for the fact that the ionization gauge and capacitance manometer were located at different points on the vacuum system, somewhat removed from the FTICR analyzer cell, a correction factor was required. This was obtained by determining the rate coefficient of a well-studied reaction ($C_3H_3^+ + C_2H_4 \rightarrow$ products, $k_{\text{ex}} = (1.0 \pm 0.3) \times 10^{-9}$ cm³/s),¹⁹⁻²⁴ where the ionization gauge pressure readings were corrected by using the capacitance manometer. This experimentally determined rate coefficient was then compared with the average of published values¹⁹⁻²² and the ratio of the published value to the measured, which was 3.3 ± 1.1 ,²⁵ was used as a correction factor. This factor was used in calculating the absolute rate coefficients reported in this article. All calculations of rate coefficients and 95% confidence limits were performed with a menu-driven Fortran computer program (available from the authors on request).

Reactive and nonreactive $C_3H_3^+$ ions were produced by charge-transfer reactions of various precursors with Xe^+ , formed with an electron beam pulse of 5-ms duration at an ionizing electron energy of ca. 15 eV. Propargyl iodide was used as a precursor for $C_3H_3^+$ in studies of the reaction of this ion with acetylene, deuterated acetylene, and diacetylene, while a number of different precursors (propargyl iodide, propargyl bromide, propargyl chloride, propyne, and allene) were used to investigate the reaction mechanisms leading to $C_5H_3^+$ ion formation. In some studies $C_3H_3^+$ ions were produced directly from the above-mentioned precursors by electron impact to compare the effect of ionization technique on the ratio of reactive to unreactive isomers.

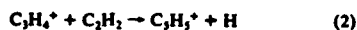
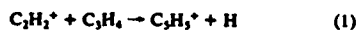
Propargyl iodide was prepared from propargyl chloride by a halogen exchange reaction.²⁶ The details of purification are given elsewhere.⁷ Propargyl chloride, propargyl bromide, allene, propyne, and acetylene were obtained commercially and their purity was checked by obtaining wide mass range spectra. In the case of acetylene, some production of protonated acetone was observed at long delay times indicating the presence of a small amount of acetone as an impurity. Propargyl bromide was distilled before use in order to remove toluene which was present as a stabilizing agent. Deuterated acetylene was prepared from D_2O and CaC_2 . Diacetylene was prepared by the method of dehydrochlorination of 1,4-dichloro-3-butyne in aqueous potassium hydroxide/dioxane solution.²⁷ All the samples were used after multiple freeze-pump-thaw cycles.

Results

$C_3H_3^+$ Reactions with Acetylene. Despite an earlier report¹³ that linear $C_3H_3^+$ is quite reactive with acetylene, only very low intensities of $C_5H_3^+$ and $C_5H_5^+$ produced via this reaction could be found in this work. Experimental conditions of the earlier study were duplicated as closely as possible, and then varied substantially with respect to relative pressures of neutrals (from 1.1 to 8.1 C_2H_2 , C_2H_2I) and overall system pressure (from 5×10^{-7} to 3×10^{-5} Torr). $C_3H_3^+$ ions were formed from propargyl chloride.

bromide, and iodide by both charge transfer using Xe^+ and electron impact. In order to determine other possible sources of C_3H_3^+ observed under the earlier reaction conditions, binary mixtures of acetylene and one of the C_3H_3^+ precursors reported^{12,13} earlier were used. Intensities of C_3H_3^+ and C_3H_2^+ were first measured after a 125-ms reaction time. Then the parent ion, C_3H_3^+ , and C_3H_2^+ were each ejected separately during the 125-ms reaction period to assess their contribution to C_3H_3^+ and C_3H_2^+ formation.

For each different neutral precursor, the sources and amounts of C_3H_3^+ ions produced were found to be different. Propyne and allene were similar in producing large amounts of C_3H_3^+ and no C_3H_2^+ ion. However, the $\text{C}_3\text{H}_3^+ + \text{C}_2\text{H}_2$ reaction was not responsible for C_3H_3^+ formation. The main reactions leading to C_3H_3^+ were



in both cases. On the other hand, when propargyl iodide, propargyl bromide, and propargyl chloride were used as precursors, relatively smaller amounts of C_3H_3^+ ion formation were observed along with C_3H_2^+ ion production. In the propargyl chloride case



were the major reactions leading to C_3H_3^+ formation. For propargyl bromide the



reaction was the only source of C_3H_3^+ ions observed. Any contribution to C_3H_3^+ formation from linear C_3H_3^+ was less than the experimental uncertainty. Finally, very little (almost negligible) amounts of C_3H_3^+ ions were observed when propargyl iodide was used as a precursor and the reactions



were the major contributors in this case. An upper limit for the rate constant, k , for reaction 7 was estimated as $5 \times 10^{-12} \text{ cm}^3/\text{s}$ by assuming that the very small C_3H_3^+ signal observed resulted from this reaction, and using the expression $[\text{C}_3\text{H}_3^+](t) = [\text{C}_3\text{H}_3^+](0) - [\text{C}_3\text{H}_3^+](t) = [\text{C}_3\text{H}_3^+](0)e^{-kt}$, where n is the C_2H_2 number density. Overall results for the production of C_3H_3^+ and C_3H_2^+ ions with different neutrals which have been reported^{12,13} as precursors of C_3H_3^+ are summarized in Table I.

Because propargyl iodide was shown to produce the highest reactive/unreactive ratio of C_3H_3^+ ions in both earlier^{12,13} and the present work (see Table II), it was as a precursor for C_3H_3^+ ions in these reaction kinetics studies. Since the precursor neutral molecule was always present in the FTICR analyzer cell, it was a competitor with the reactant neutral of interest in ion/molecule reactions involving C_3H_3^+ . In order to determine the rate coefficient of reactions of C_3H_3^+ with the neutral reactant, it was necessary first to monitor the reactions of this ion with $\text{C}_3\text{H}_3\text{I}$ and then to subtract the rate coefficient for this reaction ~~of $\text{C}_3\text{H}_3\text{I}$ and then to subtract the rate coefficient for this reaction~~ from the total rate coefficient observed in the presence of both the precursor neutral and the reactant of interest. Reactions of C_3H_3^+ with propargyl iodide ~~was~~ monitored as a function of time following charge-transfer chemical ionization of $\text{C}_3\text{H}_3\text{I}$ by Xe^+ and ejection of all ions but C_3H_3^+ reaction channels with propargyl iodide which have been reported elsewhere.⁷

Isomerization of Linear C_3H_3^+ . In addition to the absence of any significant C_3H_3^+ and C_3H_2^+ formed by reaction of linear C_3H_3^+ with C_2H_2 , it was also observed that C_2H_2 led to the isomerization of linear C_3H_3^+ ions to their cyclic form, thus rendering them unreactive toward their parent neutral ($\text{C}_3\text{H}_3\text{I}$) as well as toward C_2H_2 . This isomerization was followed as a function of C_2H_2 pressure and a direct pressure dependence was found, as can be seen in Figure 1.

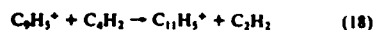
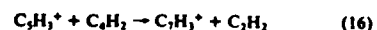
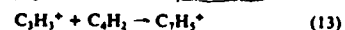
C_3H_3^+ Reactions with C_2D_2 . To achieve a better understanding of the isomerization of linear C_3H_3^+ , C_2D_2 instead of C_2H_2 was used as the neutral reactant. The following isotope exchange reactions were observed.



With the FTICR ejection capabilities, it was found that reactions 9 and 10 contribute equally to the production of C_3HD_2^+ while reaction 12 produces more of the C_3D_3^+ (80%) than reaction 11 (20%).

Ion intensity vs. time curves for the $\text{C}_3\text{H}_3^+/\text{C}_2\text{D}_2$ reaction are shown in Figure 2. The overall rate coefficient for the disappearance of C_3H_3^+ was calculated by subtracting the observed rate coefficient for the reaction with propargyl iodide from the total observed rate coefficient in the presence of C_2D_2 . This observed rate coefficient was then converted to the true rate coefficient by using the corrected pressure of C_2D_2 . A value of $(4.5 \pm 1.9) \times 10^{-10} \text{ cm}^3/\text{s}$ was found at a cell temperature of 373 K for the disappearance of C_3H_3^+ (reactions 8 and 9). In Figure 3, ion intensity vs. time curves of C_3H_3^+ are compared for reactions with and without C_2D_2 .

C_3H_3^+ Reactions with Diacetylene. After ejection of all ions except C_3H_3^+ following charge-transfer chemical ionization by Xe^+ of a mixture of diacetylene and propargyl iodide, the ion/molecule reactions as a function of time were monitored. Consecutive C_2 and C_4H_2 addition reactions observed:



Some of these product ions were seen to react further with propargyl iodide by displacement of atomic iodine:



Ion intensity vs. time curves for the $\text{C}_3\text{H}_3^+/\text{C}_4\text{H}_2$ reaction are shown in Figure 4. The rate coefficient for the disappearance of C_3H_3^+ (reactions 13 and 14, Figure 5) was calculated as described earlier, and a value of $k = (1.4 \pm 0.7) \times 10^{-10} \text{ cm}^3/\text{s}$ was found.

Propargyl iodide, bromide, and chloride were all used as precursors of C_3H_3^+ in studying its reactions with diacetylene. For each precursor, both electron impact and charge-transfer chemical ionization techniques were used. The percentages of reactive isomer in the reaction with diacetylene are shown in Table III. When these percentages of reactive isomer were compared to those in the absence of C_4H_2 (see Table II), it was clear that some isomerization of the reactive linear C_3H_3^+ ion, as well as reactions 13 and 14, had taken place (see also Figure 5). This isomerization was followed as a function of C_4H_2 pressure and a direct pressure dependence was found, as can be seen in Table IV.

Discussion

Although the results of this work are not in agreement with the earlier report¹² of $C_3H_3^+/C_3H_2$ reactivity, the discrepancy is most likely due to limitations of the older pulsed ICR¹³ instrumentation for studying ion/molecule reaction pathways in complicated systems when compared to newer FTICR capabilities. Facile ejection of all ions except the one whose ion/molecule reactions are being investigated offers a very clean monitoring opportunity for product-parent relationships even in complicated consecutive and competitive reaction systems. Various alternative pathways for the production of $C_3H_3^+$ and $C_3H_2^+$ which have been described above probably contributed significantly to the intensities of these ions seen in the earlier work. Additional support for the low reactivity of $C_3H_3^+$ with C_2H_2 is found in a recent report²⁸ of the rate coefficient for this reaction as less than 0.01×10^{-9} cm³/s, although the isomeric form of $C_3H_3^+$ was not given. It is also possible that the highest pressures used in this work did not reach those of the earlier study¹³ due to differences in the location of capacitance manometers, ionization gauges, etc. Thus third-body stabilization of $C_3H_3^+$ collision complexes might have been occurring to some extent in the earlier work and not in that reported here.

The most likely mechanism of the observed isomerization of $C_3H_3^+$ ions by collisions with acetylene is a "reactive" rather than a "nonreactive" one. That is, it results from an intimate encounter of the ion and neutral in the $C_3H_3^+$ collision complex. This hypothesis is confirmed by the fact that deuterated forms of $C_3H_3^+$ were produced when C_2D_2 was the neutral reactant (see Figure 3). In most cases the $C_3H_3^+$ collision complex dissociates to give the cyclic, unreactive, $C_3H_3^+$ isomer, instead of the reactive, linear form which reacted initially. The possibility of nonreactive collisional isomerization of linear $C_3H_3^+$ to the cyclic isomer has been ruled out because experiments at elevated pressures of xenon (to ca. 1×10^{-5} Torr) showed no interconversion. Similar interconversion of $C_3H_3^+$ ions from a linear to cyclic form has also been reported²⁹ in the reaction with C_2H_2 and has also been shown to take place via complex formation by using isotopically labeled C_2H_2 . To confirm the hypothesis that energetically less stable, reactive, (linear) $C_3H_3^+$ ions interconvert to more stable, unreactive ones, cyclic $C_3H_3^+$ ions were also reacted with C_2D_2 and no isotope exchange reactions were observed.

Plots of $C_3H_3^+$ ion intensity vs. time for reaction with diacetylene (C_4H_2) (Figure 5) indicate a 10–12% increase in the intensity of the unreactive isomer relative to the reaction when the parent precursor only is present. Isomerization of reactive $C_3H_3^+$ was also seen when different precursors were used (compare Tables II and III). A similar mechanism involving complex formation may be responsible for this isomerization as well, although it was not investigated in any detail.

The extensive ion/molecule condensation reaction sequences (reactions 13–19) observed when $C_3H_3^+$ reacts with C_2H_2 suggest that this aspect of the proposed¹⁴ ionic path to soot formation is quite credible. The rate coefficient determined in this work for $C_3H_3^+$ disappearance ($(1.4 \pm 0.7) \times 10^{-9}$ cm³/s) is in good agreement with that determined earlier¹³ ($(1.0 \pm 0.5) \times 10^{-9}$ cm³/s). Some of the product ions formed (e.g. $C_4H_3^+$ and $C_4H_4^+$) have been seen to be abundant in both nonsmoking and smoking flames.³ On the other hand, the observation of $C_3H_3^+$ isomerization and not condensation with acetylene suggests that the proposed sequential acetylene addition reactions to $C_3H_3^+$ in the ionic soot formation mechanism be reconsidered. Other channels such as direct reaction of neutral aromatics with $C_3H_3^+$ ^{3,7} may be as important in the formation of small polycyclic ions.

These experiments and those reported earlier¹³ were carried out at relatively low pressures ($p \leq 5 \times 10^{-5}$ Torr). It is thus quite possible that third-body collisions in atmospheric pressure flames can stabilize a fraction of the $C_3H_3^+$ reaction complexes before the "reactive" deactivation observed in this work can take place. However, direct bimolecular reaction of linear $C_3H_3^+$ with acetylene to form $C_4H_3^+$ and $C_4H_4^+$ does not appear to take place readily.

Reactivity studies involving other small hydrocarbon ions and flame neutrals, including determination of rate coefficients at elevated temperatures, are in progress and will be reported in subsequent publications.

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- (24) The uncertainty given is the 95% confidence limit of the mean of five determinations. Reported uncertainties for the correction factor and rate coefficients throughout this paper are also 95% confidence limits.
- (25) The large uncertainties reported for the correction factor and rate coefficients calculated using it in this work are primarily due to the wide range of reported values for the $C_3H_3^+ + C_2H_2$ reaction used to determine the correction factor. The even more widely studied "standard" calibration reaction of CH_4^+ with CH_4 could not be employed because the lowest mass-to-charge ratio accessible to the FTMS-1000 instrument is m/z 18.
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Table I: Production of $C_5H_5^+$ and $C_5H_3^+$ ions in mixtures of various neutrals and acetylene.^a

Neutral	Ionic sources ^b of $C_5H_5^+$ after Xe^+ charge transfer ionization of a mixture of the neutral and acetylene	Ratio of $C_5H_5^+$ prod. relative to that in allene case ^c	Ionic sources ^b of $C_5H_3^+$	Intensity of $C_5H_5^+$ vs. $C_5H_3^+$	Percent reactive $C_3H_3^+$ ions
Allene	$C_2H_2^+$ (40%) $C_3H_4^+$ (60%)	1.0	-	-	<5
Propyne	$C_2H_2^+$ (40%) $C_3H_4^+$ (60%)	0.75	-	-	30
Propargyl chloride	$C_2H_2^+$ (40-50%) $C_3H_3Cl^+$ (50-60%)	0.25	$C_3H_3Cl^+$ (20%) $C_3H_3^+$ (20%) $C_2H_2^+$ (60%)	3.0	15
Propargyl bromide	$C_3H_3Br^+$ (90-100%)	0.08	$C_2H_2^+$ (70%) [$C_3H_3^+$ + $C_3H_3Br^+$] (30%)	2.0	85
Propargyl iodide	$C_2H_2^+$ (40%) $C_3H_3^+$ (60%)	<0.02	$C_2H_2^+$ (50%) $C_3H_3^+$ (50%)	1.7	90

^a All ions were produced by chemical ionization charge transfer from Xe^+ .

^b Percentages show the relative contributions to $C_5H_5^+$ and $C_5H_3^+$ production as determined by double resonance experiments and have an estimated uncertainty of $\pm 10\%$.

^c Neutral reactants all had the same pressure (7×10^{-7} torr) as measured by the ionization gauge. Xenon and acetylene pressures were 5.6×10^{-6} and 1.8×10^{-6} torr, respectively.

Table II: Percentages^a of reactive $C_3H_3^+$ found from various precursors by various ionization techniques (monitored by observing reaction with the precursor neutral).

Ionizing technique	Precursor		
	Propargyl iodide	Propargyl bromide	Propargyl chloride
Electron impact (15 eV)	90%	40%	10%
Chemical ionization charge transfer with Xe^+	90%	85%	15%

^a Estimated error is $\pm 5\%$.

Table III: Percentages^a of reactive $C_3H_3^+$ observed in the reaction with C_4H_2 .^b

Ionization technique	Precursor		
	Propargyl iodide	Propargyl bromide	Propargyl chloride
Electron impact (15 eV)	75%	30%	5%
Charge transfer by Xe^+	75%	65%	5%

^a Estimated error is $\pm 5\%$.

^b $P_{C_4H_2} = 4.8 \times 10^{-7}$ torr.

Table IV: Changes in $C_3H_3^+$ reactivity^a at different pressures of diacetylene.^b

Pressure of $C_4H_2/10^{-7}$ torr	% of unreactive $C_3H_3^+$
0.8	16
1.6	17
4.8	25
7.2	32
8.0	35
9.6	40

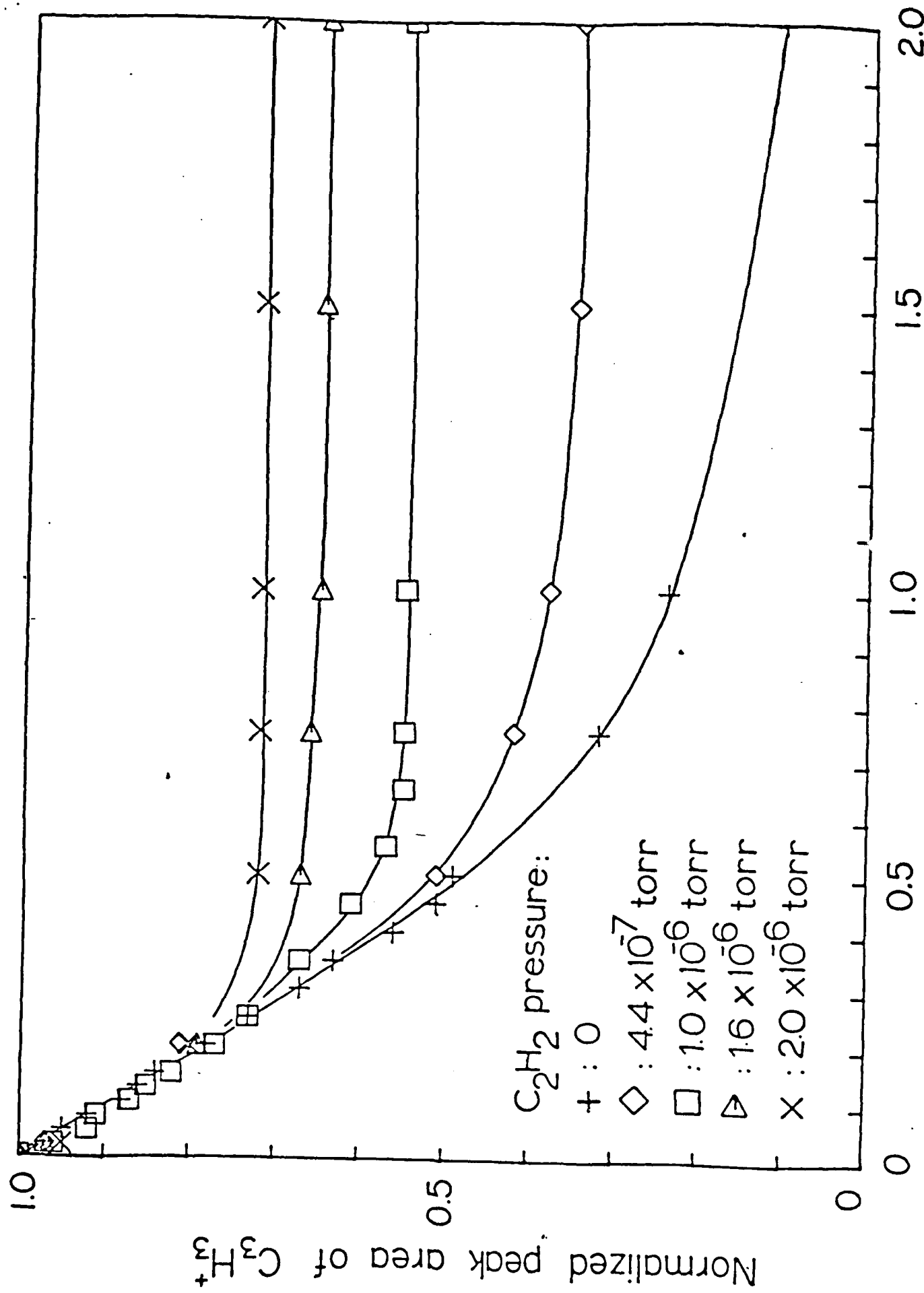
^a $1-C_3H_3^+$ ions were produced from propargyl iodide by chemical ionization charge transfer with Xe^+ . ($p_{C_3H_3I} = 1.1 \times 10^{-7}$ torr; p_{Xe} was adjusted to maintain a constant total pressure of 2.6×10^{-6} torr as read on the ionization gauge).

^b All pressures are capacitance-manometer corrected.

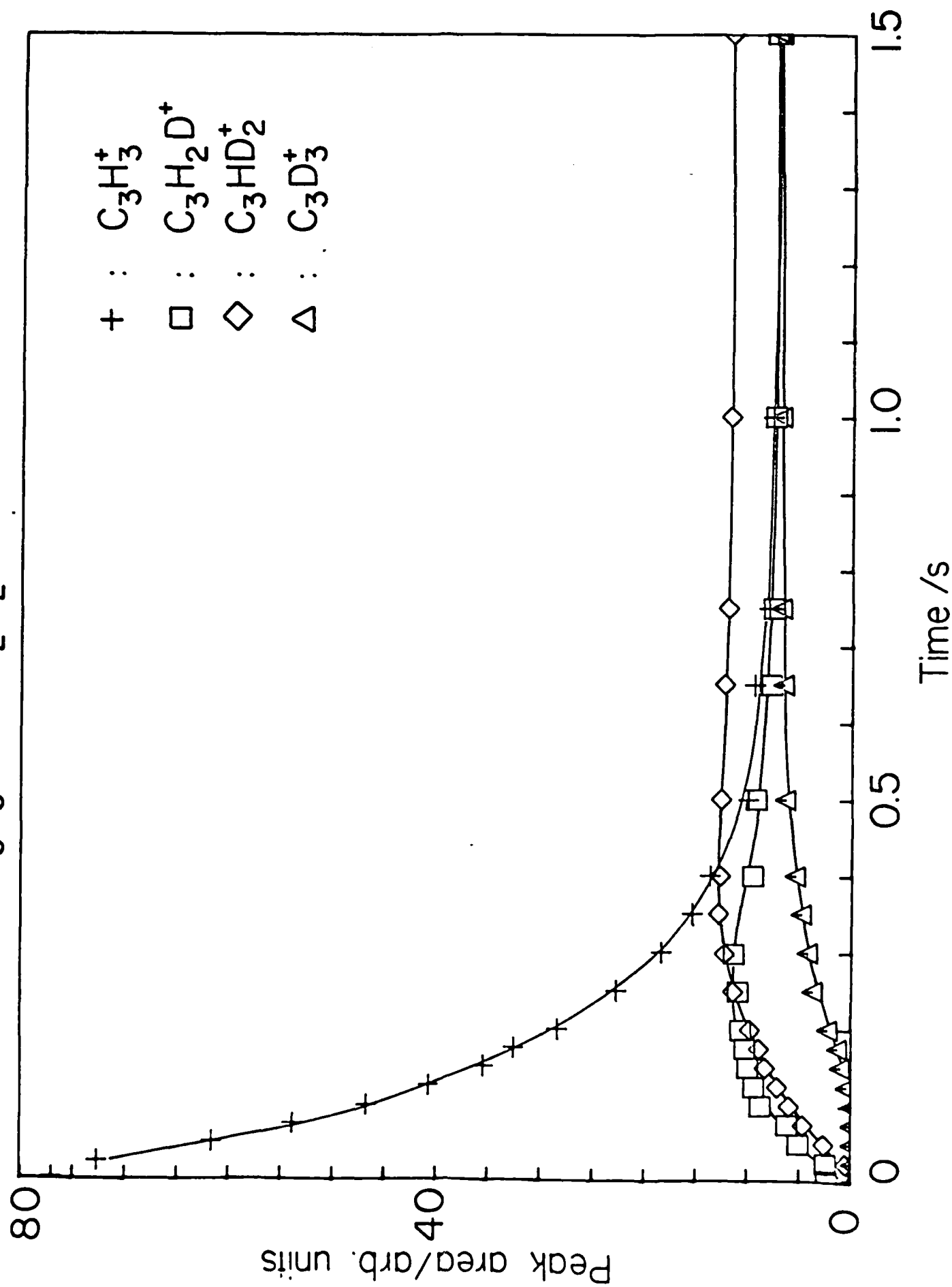
Figure Captions

- Figure 1. Isomerization of linear $C_3H_3^+$ ions at different pressures of C_2H_2 . $C_3H_3^+$ ions were produced by charge transfer reactions with Xe. $P_{C_3H_3I} = 1.1 \times 10^{-7}$ torr; P_{Xe} was adjusted to maintain a constant total pressure of 2.6×10^{-6} torr as measured on the ionization gauge. (All pressures are capacitance-manometer corrected.)
- Figure 2. Isotope exchange reactions of $C_3H_3^+$ with C_2D_2 . Disappearance of $C_3H_3^+$ ion includes reactions with propargyl iodide. Note that the sum of all isotopic forms of $C_3H_3^+$ remaining at the end of the reaction with C_2D_2 approximately equals the total unreactive $C_3H_3^+$ when C_2H_2 is used as a neutral reactant at the same pressure (see Fig. 1). $P_{C_3H_3I} = 1.1 \times 10^{-7}$ torr; $P_{C_2D_2} = 1.2 \times 10^{-6}$ torr; $P_{Xe} = 6.2 \times 10^{-6}$ torr.
- Figure 3. $C_3H_3^+$ ion decay curves for reaction with C_3H_3I and C_2D_2 . (Pressures are the same as given for Fig. 2.)
- Figure 4. Reactions of $C_3H_3^+$ with C_4H_2 . Disappearance of $C_3H_3^+$ and product ions include reactions with propargyl iodide. $P_{C_3H_3I} = 1.1 \times 10^{-7}$ torr; $P_{C_4H_2} = 4.8 \times 10^{-7}$ torr; $P_{Xe} = 6.2 \times 10^{-6}$ torr. (All pressures are capacitance-manometer corrected.)
- Figure 5. $C_3H_3^+$ decay curves for the reactions with C_3H_3I and C_4H_2 . (Pressures are the same as given for Fig. 4.)

Reactivity of $1-C_3H_3^+$ with C_3H_3I at different acetylene pressures



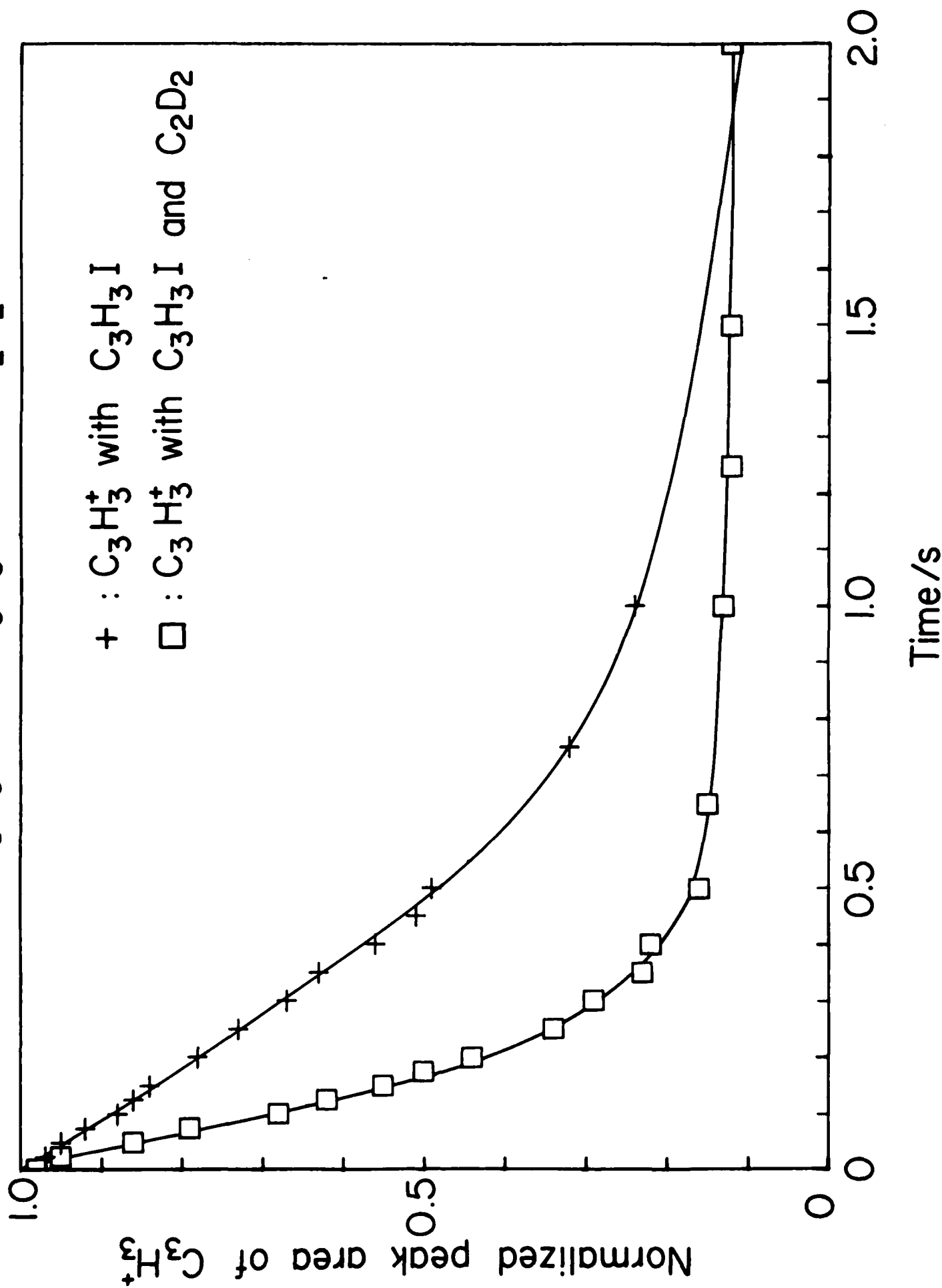
Reactions of $1-C_3H_3^+$ with C_2D_2



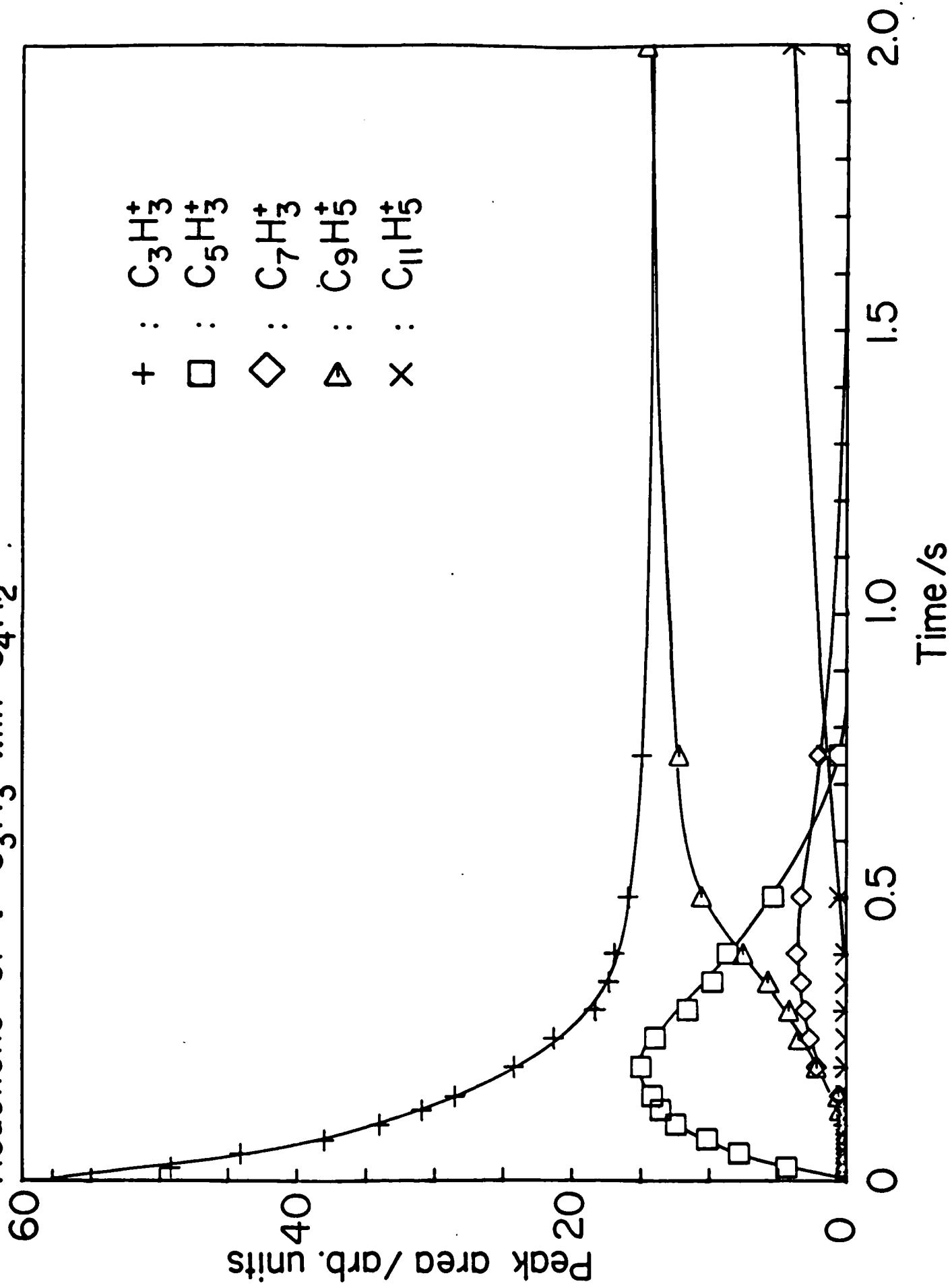
Reactions of 1-C₃H₃⁺ with C₃H₃I and C₂D₂

+ : C₃H₃⁺ with C₃H₃I

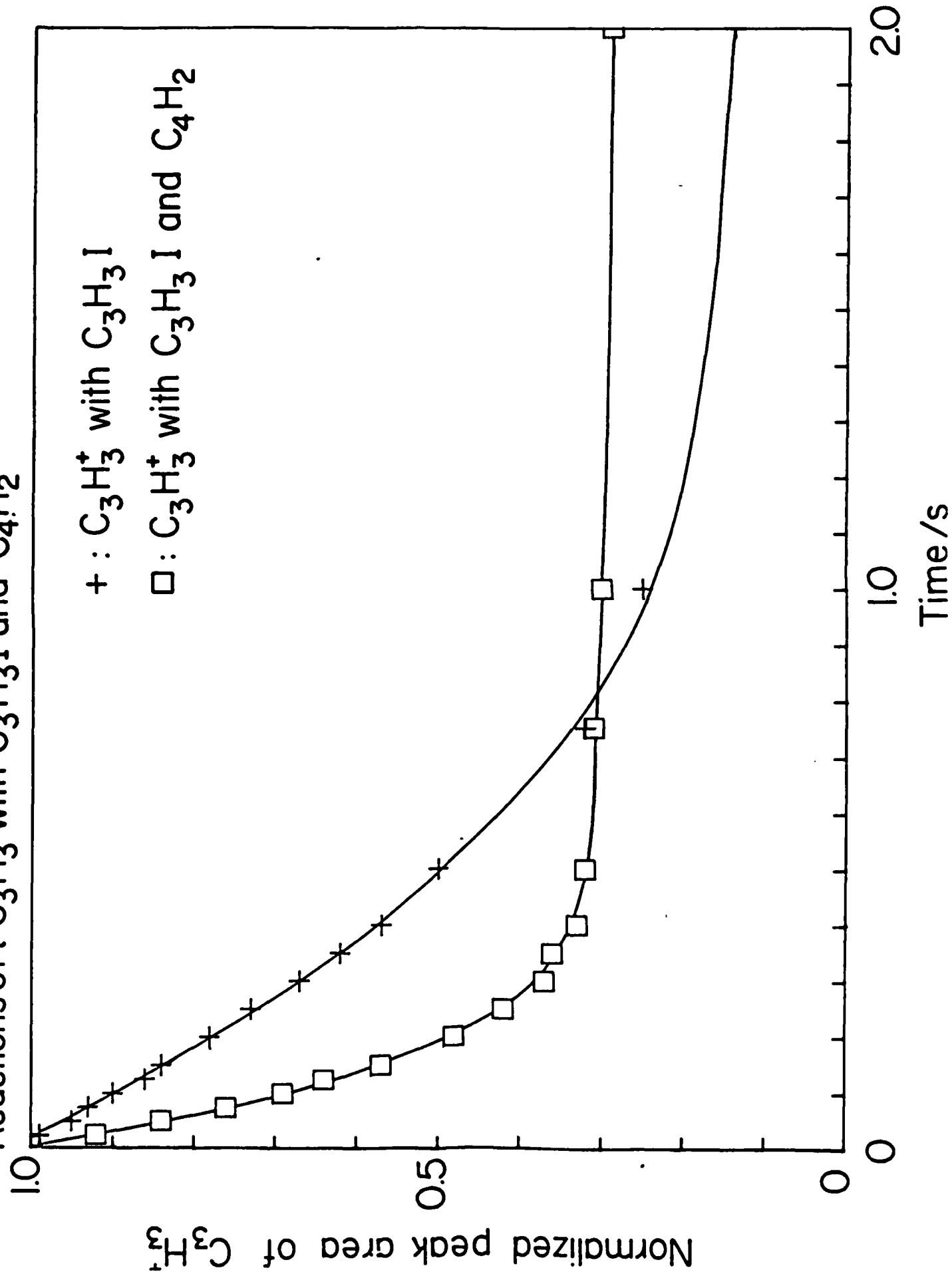
□ : C₃H₃⁺ with C₃H₃I and C₂D₂



Reactions of $1-C_3H_3^+$ with C_4H_2



Reactions of $l\text{-C}_3\text{H}_3^+$ with $\text{C}_3\text{H}_3\text{I}$ and C_4H_2



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